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Upgrading bio-oil and pretreated bio-oil by hydroprocessing in a continuous packed-bed reactor

By

Divya Reddy Parapati

A Dissertation
Submitted to the Faculty of
Mississippi State University
in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in Forest Resources
in the Department of Sustainable Bioproducts

Mississippi State, Mississippi

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Upgrading bio-oil and pretreated bio-oil by hydroprocessing in a continuous packed-bed reactor

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Bio-oil obtained by the fast pyrolysis of biomass has the potential to serve as source of alternative liquid fuel for both power generation and transportation fuel. Bio-oils are comprised of oxygenated compounds, due to the presence of a high percentage of these oxygenated groups bio-oil possesses negative properties such as low heating value, low volatility, thermal instability, corrosiveness, immiscibility with fossil fuels and a tendency to polymerize over time. Bio-oils have been converted to both boiler and transportation fuels in laboratory and demonstration projects. However, the available technologies have not proven commercially viable. Therefore, the main objective of this study is to develop additional, potentially commercializable, technologies to upgrade bio-oils and pretreated bio-oil by hydroprocessing pathways.

Previous hydrodeoxygenation studies over nearly three decades have provided considerable information about methods to upgrade bio-oil by this technology. However, rapid catalyst deactivation and low yields continue to be problematic and further research is required to refine current hydrodeoxygenation methods and catalysts. In our study we are applying pretreatment to the bio-oil at ambient temperature and pressure conditions to

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hydroprocess pretreated bio-oil in a single-stage. An initial pretreatment was performed to convert aldehydes present in the bio-oil into carboxylic acids followed by a single-stage hydroprocessing, that was performed to produce hydrocarbons. Where appropriate, successful products produced from the hydroprocessing treatments were analyzed for acid value, oxygen content, heating value, elemental analysis, FTIR and GC-MS. Statistical analysis was performed by analysis of variance (ANOVA).

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DEDICATION

I would like to dedicate this work to my parents: Sujatha Parapati and Govardhan Reddy Parapati. I would also like to dedicate this work to my brother Dheeraj Parapati and uncle Karnaker Reddy Ambati for their constant love, support and encouragement.

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CHAPTER I

INTRODUCTION

1.1 Biomass

Biomass is a renewable energy resource with negligible sulfur and nitrogen content and emits net zero CO_2 to the atmosphere. Due to these properties use of biomass has attracted interest as an alternative fuel source to supplement fossil fuels (Bridgwater et al., 1999, Battacharya et al., 2003). Liquid biofuels can be produced from biomass to increase the energy density and for convenience of use. Various methods have been developed for the conversion of biomass into useful energy. These conversion methods were shown in Figure 1.1. Biomass conversion processes includes physical conversion, biochemical conversion and thermal conversion (Goyal et al., 2008). Physical conversion involves pressing the plant or animal matter to produce triglycerides. Triglycerides cannot be used directly as transportation fuels, and require further processing. Triglycerides can be converted into biodiesel, a renewable fuel, with the transesterification process. The transesterification process converts triglycerides into fatty acid alkyl esters in the presence of alcohol (Gunawardena and Fernanado 2013).

The biochemical conversion process involves the breakdown of complex chemical compounds present in the biomass into simpler sugars or alcohols in the presence of microorganisms or enzymes. Biomass conversion into alcohols such as

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ethanol has attracted wide interest in the recent past. Ethanol can be produced from ligno-cellulosic biomass, by breakdown of cellulose into monomers in the presence of enzymes and subsequently subjected to fermentation under anaerobic conditions using microorganisms (Gunawardena and Fernanado 2013).

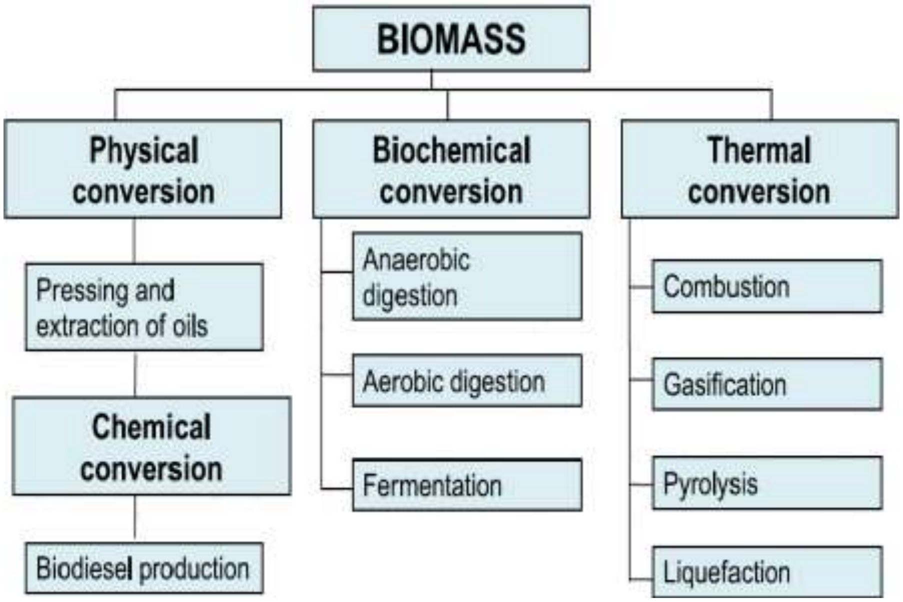

Figure 1.1 Different methods of biomass conversion.

(adapted from Gunawardena and Fernanado et al., 2013).

The thermochemical process involves chemical transformation of biomass constituents to produce energetically useful intermediate products and/ or end products in the presence of heat. The increasing demand for transportation fuels, led to the development of other processes that involve conversion of biomass into liquid and gaseous products (Li et al., 2008) such as gasification, pyrolysis and liquefaction. The gasification process converts biomass to a gaseous mixture (synthesis gas or syngas), which mainly consists of hydrogen, carbon monoxide, carbon dioxide and methane.

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Syn gas can be directly used in an internal combustion engine or can be converted to liquid fuels by a process called Fisher-Tropsch (FT) synthesis (Hayes et al., 2009, Klerk et al., 2008). Bio-oil produced by thermochemical fast pyrolysis is a liquid product with potential for production of biofuels (Xu, et al., 2009, Hew et al., 2010, Carlson, et al., 2009, Demiral, et al., 2008). Pyrolysis and liquefaction are two closely related routes and produces liquid products called bio-oil or bio-crude (Kleinert et al., 2008, Li et al., 2009). Pyrolysis, unlike gasification is performed in an oxygen-free atmosphere (Gunawardena and Fernanado 2013).

1.2 Pyrolysis

The pyrolysis process results in the thermal degradation of organic materials. This process is performed in the absence of oxygen at temperatures that typically range from 400-800 ^{o}C (Bridgwater and Cottam 1992). Char, bio-oil and non-condensable gases are formed in this process and the proportions of these products vary depending on feedstock type and the process conditions applied. (Bridgwater and Cottam 1992, Goyal et al., 2008, Sukhbaatar et al., 2009). Depending on the operating conditions, pyrolysis processes are divided into three types as shown in Table 1.1 (Demirbas 2002, Bridgwater 2012). One is slow pyrolysis, or conventional pyrolysis, and the other two are fast and flash pyrolysis. Slow pyrolysis occurs when the heating rate is relatively slow, in the range of 5 to 50 min. It is practiced to produce char as the main product, as the speed of the pyrolysis reaction determines the yield of char versus bio-oil.

At present, the preferred technology is fast or flash pyrolysis, which is performed at high temperature with very short residence time and heating rates (about 10-200 ^{o}C) and is considered as a better process than slow pyrolysis for producing liquid or gases.

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Fast pyrolysis has been investigated to maximize the yields of liquid products. The yield of bio-oil obtained from fast pyrolysis ranges from 60 to 75 dry wt% of wood, 15-20 wt% of solid char and 10-20 wt% of noncondensable gases depending on process type and conditions (Mohan et al., 2006). For production of bio-fuels, the fast pyrolysis process, by which high yields of liquid product are attained, is the necessary choice and this study was focused exclusively on the upgrading of bio-oils produced by fast pyrolysis (Mohan et al., 2006). Flash pyrolysis is an improved version of fast pyrolysis, whereby the heating rates are very high, greater than 1000 ^{o}C/s, with reaction times of a few to several seconds.

Table 1.1 Operating parameters for pyrolysis processes.

Operating parameters	Slow pyrolysis	Fast pyrolysis	Flash pyrolysis
Pyrolysis Temp (K)	550-590	850-1250	1050-1300
Heating Rate (K/s)	0.1-1	10-200	>1000
Particle Size (mm)	5 to 50	<1	<0.2
Solid Residence Time (Sec)	450-550	0.5-10	<0.5

1.3 Bio-oil

Bio-oils are dark brown liquids that are composed of a mixture of numerous chemical compounds. The bio-oil compounds result from the thermally induced molecular fragmentation of the hemicellulose, cellulose and lignin components of biomass. Bio-oils produced contain approximately 10-15% organic acids, 10-20% aldehydes, 1-4% furfurals, 1-5% ketones, 2-5% alcohols, 5-10% carbohydrates, 2-5% phenolics, 15-30% water insoluble lignin fragments and 20-30% water (Grirard and Blin 2005).

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Some chemical and physical properties of pyrolysis oils and the ASTM standard methods for testing these properties are described in Table 1.2 (Mohan et al., 2006, Czernik and Bridgwater 2004). Table 1.2 gives bio-oil heating value which typically ranges from 16-19 MJ/kg. Table 1.2 shows that a typical bio-oil has a very high acid value of 89 which is this example, with pH values below 3.0. Bio-oil contains elemental carbon (54-58 wt%), hydrogen (5.5-7 wt%), oxygen (35-40 wt%) , nitrogen (0-0.2 wt%) and sulfur (0.05 max). Bio-oil density is approximately 1.1-1.3 Kg/dm^3, and contains 45-50 wt% of oxygen that is a component of the many oxygenated compounds contained in bio-oil.

The high oxygen content of bio-oil results in thermal instability and low energy density value in comparison to petroleum fuels. The presence of high water content in bio-oil also contributes to its lower heating density, lower flame temperature and leads to ignition problems. Reduced viscosity impacts flame length, emissions and carbon efficiency. The presence of carboxylic acids results in pH values below 3.0 which in turn makes the choice of metallic vessels and processing equipment problematic. Even high-quality stainless steel materials can be corroded by exposure to bio-oil over time. As a consequence, raw bio-oils are difficult to store and transport (Czernik and Bridwater 2004).

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1.4 Bio-oil characteristics

Table 1.2 Some chemical and physical properties of pyrolysis oil.

Tests	Results	Units
Water content	15-30	mass %
pH	2.5	mass %
Acid value	89	mg KOH/g
Elemental Composition		
C	54-58	mass %
H	5.5-7.0	mass %
O	35-40	mass %
N	0-0.2	mass %
Ash content	0-0.2 max	mass %
HHV	16-19	MJ/kg
Viscosity at 40 ^{oC}	40-100	mm2/sec
Density at 20 ^{oC}	1.1-1.3	kg/dm3
Solids	0.2-1.0	mass %
Oxygen content	45-50	mass %

(Mohan et al., 2006, Czernik and Bridgwater 2004)

In comparison to fossil fuels, bio-oils emit low levels of nitrogen oxide and sulphur dioxide on combustion and are considered as CO_2 neutral. Raw untreated bio-oil can be suitable as boiler fuel.

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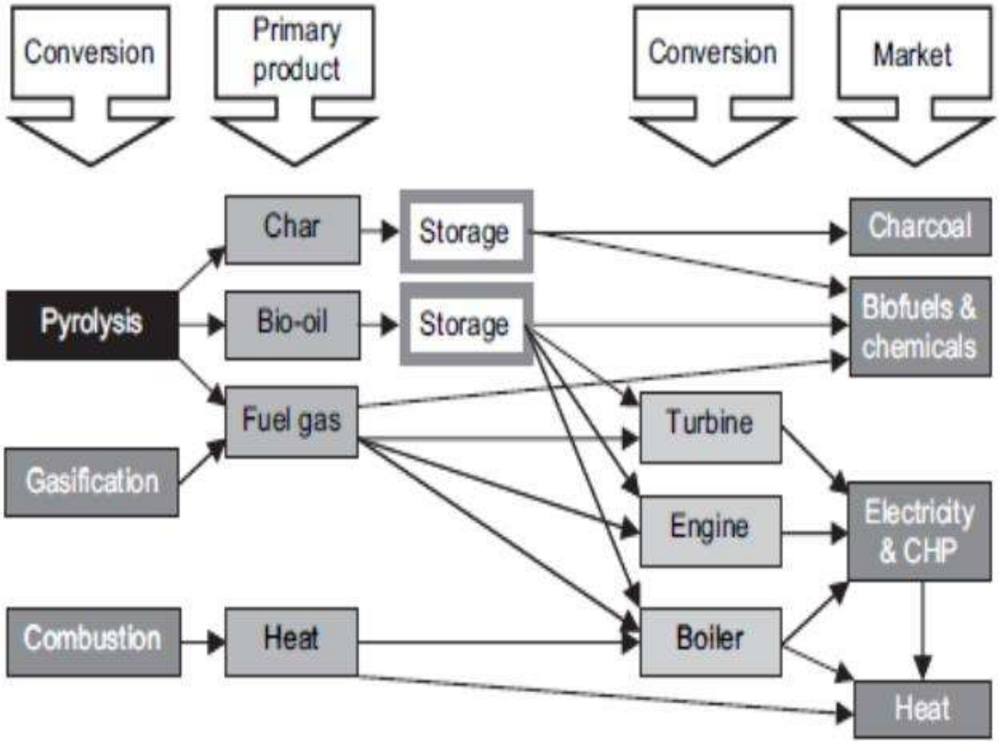

Figure 1.2 Different industrial applications of bio-oil.

(adapted from Bridgwater et al., 2012).

The American Society for Testing and Materials (ASTM) has recently published a “Standard Specification for Pyrolysis Liquid Biofuel” (ASTM D7544-10) (ASTM 2010) that provides grades for pyrolysis liquid biofuels from biomass for combustion in industrial burners. This standard provides a means to rate bio-oils for combustion as boiler fuels with regard to quality. ASTM D7544-10 is a performance standard with no specification as to methods of production to produce the rated products.

The boiler fuel grades are determined by characteristics such as heating value, water content, solids content, viscosity, density, sulfur content, ash content, flash point and pour point. Higher bio-oil fuel grades will have higher heat of combustion and pour

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point. The higher grades will also have lower water content, solids, sulfur, ash and flash point. Different industrial applications of bio-oil are shown in Figure 1.2.

Raw bio-oil has been combusted in diesel engines, both neat and as emulsions containing petroleum fuels. Raw bio-oil has also been tested in turbines and Stirling engines for the production of electricity. With the exception of the Stirling engine test researchers detected engine corrosion, deposits and significant wear (Bridgwater et al., 1999). While there was no damage to the Stirling engine the electrical generation efficiency was low. It is currently universally agreed that bio-oils must be upgraded prior to their utilization as engine fuels (Mohan et al., 2006, Elliot 2007, Furimsky 2000).

1.5 Bio-oil upgrading

Woody biomass is a renewable and zero net carbon dioxide emission energy source. For energy production, biomass can be utilized by various conversion processes such as direct combustion, fermentation, gasification, pyrolysis, and liquefaction. However, biomass utilization in the form of liquid fuel is of particular interest due to its high energy density, ease of transport and lower handling cost. Bio-oil obtained by the fast pyrolysis of biomass has the potential to serve as a source of alternative liquid fuel for both power generation and transportation fuel.

Bio-oils are comprised of oxygenated compounds such as ketones, aldehydes, carboxylic acids, esters, ethers, phenolic derivatives and aliphatic and aromatic alcohols. Largely due to the presence of a high percentage of these oxygenated groups bio-oil possesses negative properties such as low heating value, low volatility, thermal instability, corrosiveness, immiscibility with fossil fuels and a tendency to polymerize over time.

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A number of upgrading methods have been proposed to produce high-quality fuels from bio-oils. Some of them include hot gas filtration (Baldwin et al., 2013), emulsification (Chiaramonti et al., 2003, Ikura et al., 2003) and addition of additives such as low viscosity alcohols, which can reduce the initial viscosity of bio-oil and lowers viscosity increase during aging (Diebold 1997, Oasmaa et al., 2003, Qiang et al., 2008, Boucher et al., 2000). The commonly used additives were ethyl acetate, acetone, methanol, ethanol and isopropanol (Diebold et al., 2000, Diebold 1997, Oasmaa et al., 2003, Czernik et al., 1994). However, these methods will lead to improve bio-oil quality and stability with respect to storage and transportation, but not to deoxygenation completely. The recent upgrading techniques are catalytic hydroprocessing (Elliott, 2007), esterification (Tang et al., 2008, Xu et al., 2010, Xiong et al., 2009), olefination (Zhang et al., 2011, Zhang et al., 2013, Chatterjee et al., 2013), catalytic pyrolysis (French and Czernik 2010, Aho et al., 2007), hydrodeoxygenation (HDO) (Elliot 2007, Wildschut et al., 2009, Senol et al., 2005), steam reforming (Wang et al., 1996, Galdamez et al., 2005), decarbonylation and decarboxylation (Mortensen et al., 2011). Hydrodeoxygenation (HDO) has been studied extensively for conversion of bio-oil to liquid hydrocarbons.

Bio-oils have been converted to both boiler and transportation fuels in laboratory and demonstration projects. However, the available technologies have not proven commercially viable. Therefore, the main objective of this study is to develop additional, potentially commercializable, technologies to upgrade bio-oils. Fast pyrolysis is a means to produce a bio-oil from biomass. Researchers have shown that the negative properties of raw bio-oil prevent their direct use as fuels. Hydrodeoxygenation (HDO) has become a

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major method for producing hydrocarbons from bio-oil that are suitable for heating and transportation fuels. HDO is traditionally performed in two stages: a hydrotreating step at low temperature to prevent polymerization of bio-oil from thermal exposure followed by a hydrocracking step at a higher temperature to produce the final 100% hydrocarbon mixture.

Previous hydrodeoxygenation studies over nearly three decades have provided considerable information about methods to upgrade bio-oil by this technology. However, rapid catalyst deactivation and low yields continue to be problematic and further research is required to refine current hydrodeoxygenation methods and catalysts. In our study we performed pretreatment of bio-oil at ambient temperature and pressure conditions to hydroprocess pretreated bio-oil in a single-stage. An intial pretreatment has been performed to convert aldehydes present in the bio-oil into carboxylic acids followed by a single-stage hydroprocessing to produce hydrocarbons. Where appropriate, successful products produced from the hydroprocessing treatments were analyzed for acid value, oxygen content, viscosity, heating value, elemental analysis, FTIR and GC-MS. Statistical analysis was performed by analysis of variance (ANOVA) and complete mass balances were developed for successful reactions. Our studies employed a pretreated bio-oil (PTBO) upgraded by hydroprocessing to liquid hydrocarbons. The results showed that PTBO is a better feedstock, compared to raw bio-oil, in terms of producing higher yields of liquid hydrocarbons and has the potential for prolonging catalyst life (increased run time).

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1.6 Objectives

The main objective of this study is to perform bio-oil and pretreated bio-oil upgrading utilizing a continuous packed-bed reactor in the presence of pressurized hydrogen by a single-stage hydroprocessing treatment. This study mainly focuses on finding a suitable catalyst with optimum reaction conditions to hydroprocess bio-oil and pretreated bio-oil to hydrocarbon fuel.

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CHAPTER II

CATALYST SCREENING FOR CATALYTIC HYDROPROCESSING OF BIO-OIL IN A CONTINUOUS PACKED-BED REACTOR

2.1 Abstract

Fast pyrolysis of biomass produces a liquid product termed pyrolysis oil which is also frequently refered to as bio-oil. Bio-oil is a potential energy source for production of biofuels as an alternative to fossil fuels. Bio-oils are not directly applicable as transportation fuels due to the presence of oxygenated components in their composition. The objective of this study was to test several catalysts to produce organic fractions from single-stage hydroprocessing of bio-oil in a continuous packed-bed reactor. Six catalysts, four different reduced catalysts (Ni/Si-Al, CoMo/γ-Al_2O_3, NiW/Si-Al, FeW/Si-Al) and two sulfided catalysts (CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3) were tested. A range of process parameters including temperatures ranging from 375-400 °C, 1000 psig hydrogen pressure, hydrogen flow rate of 500 ml/min and at a liquid hourly space velocity of 0.5 h^{-1} were applied. The results from sulfided catalytic experiments were superior in comparison to reduced catalysts. Sulfided CoMo/γ-Al_2O_3 catalyst demonstrated the highest catalytic activity among the catalysts tested. Sulfided CoMo/γ-Al_2O_3 catalyst produced an organic fraction having a higher heating value of 41.0 MJ/kg, acid value of 5.4 mg KOH/g oil, a total water content of 1.5% and the oxygen content was reduced from 54.7 wt% in the raw bio-oil to 7.0 wt% in the hydrocarbon fraction. The organic

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fraction was also analyzed by detailed hydrocarbon analysis, simulated distillation, GC-MS and FTIR analysis.

2.2 Introduction

Biomass is an attractive feedstock for partial replacement of combusted fossil fuel for energy production. Wood and other forms of biomass including energy crops and agricultural and forestry wastes are some of the main available resources and account for 14-15% of total current energy consumption (Bridgwater 2012, Demirbas 2007, Xu et al., 2010). Fossil fuels have been shown to release large amounts of CO_2 which have been proven to increase climate warming. Biomass is a renewable material which has a negligible content of sulfur, nitrogen and ash, and decreased carbon dioxide emissions (Xu et al., 2010, Zheng et al., 2011, Mckendry 2002).

Conversion of biomass and its utilization depends upon its chemical constituents and physical properties. Biomass contains varying amounts of cellulose, hemicellulose and lignin (Goyal et al., 2008, Mohan et al., 2006). Cellulose is the largest fraction of biomass followed by hemicellulose, lignin, ash and others (Bridgwater 1999, Ana Rita 1996). Cellulose is a linear polymer consisting of beta-(1,4) D-glucopyranose units, in which the units are linked 1-4 in the alpha-configuration, with a high molecular weight of around 10^6. Cellulose comprises approximately 40-50% of dry wood (Rowel 1984).

Hemicellulose is a second major biomass chemical constituent, also known as polyose. It accounts for 25-35% of dry wood matter, 28% in softwoods and 35% in hardwoods (Rowel 1984). It consists of a mixture of polysaccharides, composed mostly of sugars such as glucose, mannose, xylose and arabinose and methylglucoronic and galacturonic acid residues. The average molecular weight of hemicellulose is less than

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30,000. Lignin is the third major component of wood and accounts for 23-33% of the softwood mass and 16-25% of the mass of hardwoods (Bridgwater 2004). Lignins are highly branched, substituted mononuclear aromatic polymers in the cell walls of most biomass types. Lignin consists of an irregular array of variously bonded hydroxyl and methoxy substituted phenylpropane units (McCarthy et al., 2000). The three monomeric phenylpropane units show the *p*-coumaryl, coniferyl and sinapyl structures.

Biomass can be treated in different ways to convert it into more valuable forms. These methods include physical conversion, biochemical conversion and thermal conversion. The various routes of biomass thermochemical conversion processes are usually classified into combustion, gasification, liquefaction, hydrogenation and pyrolysis processes. (Augustinova et al., 2013, Goyal et al., 2008). Among these processes pyrolysis has received special attention as it directly converts the biomass into solid, liquid and gaseous products by thermal decomposition, performed in the absence of oxygen. Fast pyrolysis of biomass produces a liquid termed pyrolysis oil which is usually referred to as bio-oil. Bio-oil is dark brown in color with a smoky odor. The yield of bio-oil obtained from fast pyrolysis typically ranges from 60 to 75 dry wt% of wood depending on feedstock composition, process type and conditions (Mohan et al., 2006).

Bio-oils are dark brown liquids, that are composed of a mixture of numerous chemical compounds. The many bio-oil compounds result from the thermally induced molecular fragmentation of the hemicellulose, cellulose and lignin components of biomass. Bio-oils contain approximately 10-15% organic acids, 10-20% aldehydes, 1-4% furfurals, 1-5% ketones, 2-5% alcohols, 5-10% carbohydrates, 2-5% phenolics, 15-30% water insoluble lignin fragments and 20-30% water (Grirard and Blin 2005).

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Raw untreated bio-oil can be suitable as boiler fuel. The American Society for Testing and Materials (ASTM) has recently published a "Standard Specification for Pyrolysis Liquid Biofuel" (ASTM D7544-10) (ASTM 2010) that provides grades for pyrolysis liquid biofuels from biomass for combustion in industrial burners. This standard provides a means to rate bio-oils for combustion as boiler fuels with regard to quality. ASTM D7544-10 is a performance standard with no specification as to methods of production to produce the rated products. The boiler fuel grades are determined by characteristics such as heating value, water content, solids content, viscosity, density, sulfur content, ash content, flash point and pour point. Higher bio-oil boiler fuel grades have higher heat of combustion and pour point. The higher grades also have lower water content, solids, sulfur, ash and flash point.

Raw bio-oil has been test combusted in diesel engines, both neat and as emulsions containing petroleum fuels or as diesel fuels in which bio-oil is fed in to the engine simultaneously with a fossil fuel. Raw bio-oil has also been tested in turbines and Stirling engines for the production of electricity. With the exception of the Stirling engine test researchers detected engine corrosion, deposits and significant wear (Bridgwater et al., 1999). While there was no damage to the Stirling engine the electrical generation efficiency was low. It is currently universally agreed that bio-oils must be upgraded prior to their utilization as engine fuels (Mohan et al., 2006, Elliot 2007, Furimsky 2000).

Currently tested upgrading techniques include hydrodeoxygenation (Pindoria et al., 1997; Pindoria et al., 1998., Zhang et al., 2003, Sandra et al., 1994, Senol et al., 2005), catalytic cracking of pyrolysis vapours (Nokkosmaki et al., 2000), steam reforming (Wang wt al., 1997; Wang et al., 1998), emulsification (Chiaramonti et al.,

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2003), chemical extraction, esterification (Zhang et al., 2006; Xu et al., 2006) and olefination (Zhang et al., 2011; Zhang et al., 2013, Chatterjee et al., 2013). Other studies that involve removal of oxygen in the form of CO or CO_2 are by decarbonylation and decarboxylation reactions by thermal or catalytic processes (Mercarder et al., 2010). However, oxygen removal greater than 10% was found to be difficult with these techniques.

Catalytic hydrodeoxygenation (HDO) of pyrolysis oil has received more attention (Elliot 2007, Elliot et al., 2009, Conti, 1997, Kaiser 1997, Rep et al., 2006) and it has been investigated by many researchers as a means to upgrade bio-oil. The HDO process removes oxygen from bio-oil in the presence of hydrogen pressure and a catalyst at elevated temperature. The HDO process removes the oxygenated compounds present in bio-oil by supplying hydrogen to be catalyzed with bio-oil oxygen to produce water that is immiscible in the hydrocarbon mixture. A simplified schematic of the HDO process is given in Equation 1 (Wildschut, 2009).

$$(CH_2O)\text{-} + H_2 \longrightarrow (CH_2)\text{-} + H_2O \qquad \text{Eq. 2.1}$$

Currently, HDO of bio-oil has employed well-known hydrotreating catalysts traditionally applied in the petroleum industry HDS process. Some of the catalysts include sulfided catalysts ($CoMo/Al_2O_3$ and $NiMo/Al_2O_3$), noble metal catalysts (Pd/C, Pt/C, Pt/Al, Ru/C and Ru/Al) and zeolites material (ZSM-5, MCM-41 and SUZ-4). During hydroprocessing of bio-oil, several reactions take place such as hydrodeoxygenation, decarboxylation, decarbonylation, hydrogenation, hydrogenolysis, cracking/hydrocracking and polymerization reactions leading to the formation of coke on

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the catalyst (Elliot 2007, Furimsky 2000, Huber et al., 2006). An extensive in-depth review of bio-oil hydroprocessing research was published by Elliott in 2007.

Pacific Northwest National Laboratory (PNNL) researchers initially performed tests on liquefaction products rather than fast pyrolysis bio-oil and screened 22 catalysts to determine their potential for HDO. The researchers selected CoMo 0402/S, HT 400/S and Ni-1404 as the most promising hydrotreating catalysts for further testing. The nickel catalyst showed performance similar to that of sulfided CoMo catalyst, but produced high gas yields and consumed a high amount of hydrogen. Researchers also observed that the catalytic activity of the nickel catalyst was lost after several hours of testing (Elliott 2007).

PNNL researchers performed further studies with HT 400/S catalyst to compare its performance on a liquefied bio-oil containing primarily cyclic ketones and single-ring phenolics and a second liquefied bio-oil containing primarily multi ring phenolics at a temperature of 398 °C and 13.8 Mpa of pressure. In these tests researchers obtained a light hydrocarbon product from the first liquefied bio-oil, but in the case of the second liquefied bio-oil, the alkaline content of the oil deposited on the catalyst over a 48 h test resulted in deactivation of the catalyst and reactor blockage. Based on these results researchers hypothesized that a two-stage process may reduce bio-oil polymerization that cause the tar formation and subsequent catalyst coking (Elliott 2007).

PNNL also tested a new HDO catalyst CoMo/γ-Al_2O_3 that was reported in a 1993 patent (Baker and Elliot 1993) utilizing a two-stage hydroprocessing treatment based on their earlier hypothesis cited above. An intial hydrotreating 1st-stage treatment was employed at mild temperature conditions of 180 to 240 °C, and a 2nd-stage hydrocracking

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treatment was then employed at temperatures of 300 to 400 °C. This two-stage process eliminated problems of early polymerization of the bio-oil and the reactor blockage previously experienced (Elliott 2007). This was achieved by the 1st-stage process partially hydrotreating the bio-oil to reduce water and oxygen content and producing some hydrocarbon content in the hydrotreated product. This partial upgrading allowed a higher 2nd- stage treatment to be applied at higher temperature without bio-oil polymerization, rapid catalyst coking and reactor blockage. This 2nd-stage treatment has become the standard method practiced by nearly all researchers since the Baker and Elliot (1993) discovery.

Elliot (2007) also reported on catalytic hydrotreatment performed by Veba Oel AG. Veba Oel AG performed a single-stage HDO treatment at temperatures below 300 °C. Tests were performed in a continuous feed bench-scale reactor at 17.8 MPa of pressure and temperatures of 350 to 370 °C over sulfided CoMo and NiMo catalysts. In this process researchers obtained bio-oil yields ranging from 30 to 35% with deoxgenation rates ranging from 88.0 to 99.9%. However, in this process the catalyst was deactivated relatively quickly and the formation of gum-like deposits blocked the reactor. It was also evident, that the application of a single-stage treatment was not a viable approach for CoMo and NiMo catalysts.

Elliott et al. (2009) describes PNNL research in which both hydrotreatment and hydrocracking were combined within the same hydroprocessing reactor with two levels of temperature maintained in the catalyst bed, so that both the hydrotreating and hydrocracking steps were performed without separation of intermediate products to prevent loss and treatment cost of the material. In this process bio-oil from four

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feedstocks were consecutively hydrotreated and hydrocracked with Pd/ C catalyst. Hydrotreating was applied at a temperature range of 340 to 370 °C for 35 h, and hydrocracking was performed at 400 °C. Researchers observed no coke formation. However, with the later application of a higher flow rate performed between 30 to 40 h at 340 °C the hydroprocessing reactor plugged. The researchers hypothesized that when both hydrotreatment and hydrocracking were combined at appropriate temperatures within the same hydroprocessing reactor the carbon loss in the byproduct water stream was minimized. However, the system requires a low flow rate to result in successful production of hydrocarbons.

Williams and Horne (1995) investigated the upgrading of biomass pyrolysis oils in a fluidized bed reactor at 550 °C with Na-ZSM-5, HZSM-5, Y-zeolite catalysts and activated alumina. Among these catalysts tested, HZSM-5 catalysts produced the highest yields of hydrocarbons in comparison to Na-ZSM-5, Y-zeolite and activated alumina catalysts. Upgrading of bio-oil over zeolites produced liquid hydrocarbons which were suitable as fuels but the yields were low and the catalysts deactivated rapidly due to catalyst coking.

Adjaye and Bakhshi (1995) performed the upgrading of bio-oil in a fixed-bed micro-reactor with HZSM-5, silicalite, H-modernite, H-Y and silica-alumina catalysts at temperatures ranging from 330 to 410 °C. Among these catalysts tested, HZSM-5 was the best performing catalyst in terms of yield and production of aliphatic hydrocarbons and aromatic hydrocarbons and it also produced minimum coke formation. As for the Williams and Horne (1995) results, upgrading of bio-oil over zeolites produced liquid

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hydrocarbons which are suitable as fuels but the yields were low and the catalysts deactivated rapidly due to catalyst coking.

Echeandia et al. (2010) investigated the effect of oxides of W and Ni–W catalysts on active carbon support for 1 wt% phenol hydrodeoxygenation in n-octane in a fixed-bed reactor at temperatures ranging from 423 to 573K at 15 bar of pressure. Researchers found that the incorporation of Ni on the W on active carbon resulted in better catalytic performance and that the Ni-W also minimized coke formation compared to W oxide alone.

Wildschut and Heeres (2009, 2010) performed research on HDO of bio-oil with several catalysts. Ru/Al_2O_3, Ru/C, Ru/TiO_2, Pd/C, Pt/C; sulfided $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ were screened for comparable efficacy. However, the cost of the ruthenium-based catalyst is high. Also, the 4 h reaction time is much longer than reported for other successful hydrotreating catalysts. These two factors will increase both the capital and variable costs involved in applying the Ru/C catalyst for bio-oil hydrotreating. It is likely that these high costs will render this catalyst uneconomic for bio-oil hydrotreating.

Elliott et al. (2012) reported on two-stage catalytic hydroprocessing of pine fast pyrolysis oil in a bench scale continuous-flow fixed-bed catalytic reactor system to evaluate the performance of fully sulfided catalyst beds including both ruthenium and promoted molybdenum. A two-stage treatment was employed at a temperature of approximately 170 ^{o}C and at an LHSV of 0.19 with sulfided Ru/C catalyst. This was followed by a 2nd-stage hydrocracking treatment at a temperature of 400 ^{o}C for the same LHSV with both sulfided CoMo and NiMo. The HDO was operated for 90 to 99 h depending on the catalyst type. The hydroprocessed product had densities of 0.82 to 0.92

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g/ml, oxygen content ranging from 0.2 to 2.7 wt%, and total acid number ranged from 0.01 to 2.7 mg KOH/g. However, catalyst bed plugging and pressure drop increase resulted from char particles plugging the catalyst bed. Researchers concluded that pre-filtration of bio-oil will be required for fixed-bed hydroprocessing to prevent reactor plugging.

Non-sulfided, non noble catalysts have also been tested for the catalytic hydrotreatment of pyrolysis oil. Xu et al. (2010) tested reduced NiMo/γ-Al_2O_3 for the hydrotreatment of bio-oil, obtained from fast pyrolysis of pine sawdust at mild conditions of temperature 373 K and 3 MPa hydrogen pressure. In this, study researchers also investigated the effect of Mo promoters on model compound acetic acid at temperature of 473 K and 3 MPa pressure. Zhao et al. (2012) tested the bifunctional Ni/HZSM-5, consisting of 20% Ni and Si-Al ratio of 45 for the hydrodeoxygenation of n-hexane-extracted crude bio-oil at 573 K and 5 MPa pressure in the presence of substantial concentrations of water in a cascade reaction to convert n-hexane extracted crude bio-oil into C_5 to C_9 range hydrocarbons.

Ardiyanti et al. (2012) tested the non-sulfided bimetallic Ni-Cu//γ-Al_2O_3 catalyst with varying proportions of Ni of Cu ratios for the catalytic hydrotreatment. Researchers tested both batch and the continuous reactor treatments, utilizing the pyrolysis oil in the batch reactor and the model compound anisole oil in the continuous reactor. The catalytic hydrotreatment of anisole was performed in a continuous reactor at a temperature of 300 ^{o}C and 10 bar pressure. Among the tested varying proportions of Ni and Cu, Ni to Cu ratio of 8 (16Ni2Cu) showed the highest conversion of anisole (78.6 mol%) with low leaching and coking levels. The batch reactor experiment applied 150 ^{o}C temperature for

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a time period of 1 h, followed by hydrotreatment at a temperature of 350 °C for a time period of 3 h, at 200 bar total pressure. The obtained product had an oxygen content ranging between 10 and 17 wt%, and the product properties were improved in comparison to the feed. The highest catalytic activity was observed for 16Ni2Cu (based on hydrogen uptake). Coke deposition was lower on bimetallic Ni-Cu catalyst than for the monometallic Cu catalysts.

Well known catalysts that have been tested for the hydrotreatment of pyrolysis oil include conventional hydrodesulfurisation catalysts such as sulfided CoMo/γ-Al_2O_3, NiMo//γ-Al_2O_3, and NiMo/γ-Al_2O_3-SiO_2 (Ferrari et al., 2002, Maity et al., 2000). Other catalysts such as CoMo/C (Ferrari et al., 2001, Ferrari et al., 2002), Mo supported on TiO_2, ZrO_2 and TiO_2-ZrO_2 mixed oxides (Satterfied and Yang, 1983, Lee and Ollis, 1984) have been tested as well.

From the above studies researchers concluded that the bio-oils obtained by fast pyrolysis of biomass may be converted to hydrocarbons that have the potential to serve as an alternative source for transportation fuels. However, rapid catalyst deactivation and low yields continue to be drawbacks in the HDO process. Therefore, further research is required to optimize the current HDO methods and catalysts.

The present study focused on testing various catalysts for the direct hydroprocessing of bio-oil in a continuous packed-bed reactor. Six different catalysts were screened. These catalysts include four reduced catalysts (Ni/Si-Al, NiW/Si-Al, FeW/Si-Al and CoMo/γ-Al_2O_3) and two sulfided catalysts (CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3). The best performing catalysts were further tested on pretreated bio-oil feed.

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2.3 Experimental

2.3.1 Materials

Bio-oil was produced by the fast pyrolysis process at a temperature of 400-450 °C under nitrogen gas atmosphere using a 7 kg/h auger-fed pyrolysis reactor located in the Department of Sustainable Bioproducts, Mississippi State University.

2.3.2 Catalysts

Catalyst supports such as Si-Al, γ-alumina and the required inorganic metal salts for preparation of Ni/Si-Al (25% Ni), NiW/Si-Al (10% Ni, 5% W), FeW/Si-Al (5% Fe, 5% W) and NiMo/γ-Al_2O_3 (5% Ni, 15% Mo), catalysts were commercially purchased from Alfa Aesar, Sigma Aldrich and Fisher Scientific. The Ni/Si-Al, NiMo/γ-Al_2O_3, NiW/Si-Al, and FeW/Si-Al catalysts were prepared by the wet-impregnation method, whereby the metal salts were impregnated on catalyst supports and then dried at 120 °C for 4-6 h before being calcined at 550 °C for 4 h. The calcined metal-dispersed catalysts were then reduced at 700 °C using hydrogen flow (100 ml/m) for 4 hr. CoMo/γ-Al_2O_3 was purchased from Alfa Aesar. Cyclohexane and carbondisulfide were purchased from Fisher Scientific. The oxide form of catalysts were activated by subjecting them to a sulfidation process prior to the hydroprocessing experiments. CoMo/γ-Al_2O_3 and NiMo/ γ-Al_2O_3 were sulfided with a solvent mixture of 2 vol% carbon disulfide and cyclohexane. To 800 ml of cyclohexane solvent, 16 ml (2 vol%) of carbon disulfide was added and the solvent mixture was pumped through a high-pressure dual-pump system. Sulfiding of the catalyst was performed at 300 °C, a pressure of 750 psi and LHSV of 1 h^{-1} for a period of 4 h.

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2.3.3 Continuous packed-bed reactor

The continuous packed-bed reactor (Figure 2.1) used in the experiments consisted of a 1” I.D tubular reactor enclosed in a three-zone furnace (three 6” zones each independently controlled by its own temperature controller) followed by a condensation system. The temperatures inside the reactor were monitored with a point profile thermocouple equipped with ten sensing points (Omega Instruments). Three temperature sensing points were located in each of the 3 reactor heater zones for a total of 9. The tenth temperature sensing point was located at the condenser orifice. The catalyst bed temperature zones were maintained as closely as possible to the desired temperature set point through the course of the experiment. The catalytic reaction is exothermic such that temperatures are difficult to control due to the adiabatic nature of the reaction. Temperature controlled within a temperature range of 375-400 °C was possible. The bio-oil was pumped into the catalyst tube with a high pressure dual-pump system (Teledyne Isco 500D). The hydrogen flow rate was controlled with a mass flow controller (MFC; Brooks Instruments), and the reactor pressure was controlled with a back-pressure regulator. A schematic diagram of the reaction is shown in Figure 2.1.

For all experiments the reactor was loaded with catalyst at a temperature initially set to 150 °C. Figure 2.1 shows a diagram of the schematic of the continuous packed- bed reactor. Figure 2.2a and 2.2b shows the method of catalyst loading in the continuous packed-bed reactor. Once this initial temperature set point was attained, the reactor temperature was raised by another 100 °C upon reaching the resultant temperature of 250 °C and the reactor temperature was again raised to 350 °C. A final 25 to 50 °C increase was often applied to raise the actual reaction temperature as close to 375 °C as possible.

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The reactor was pressurized to the desired 1000 psi hydrogen reaction pressure. After attaining the temperature of approximately 375 °C, the desired pressure of 1000 psi hydrogen was supplied to the reactor by a mass flow controller (MFC) producing a desired flow rate of 500 ml/min.

All experiments were performed at a LHSV of 0.5 h^{-1}. The exit gas flow rate in milliliters per minute (ml/min) was monitored by an Agilent gas flow meter. Products exiting from the packed-bed reactor were cooled in the condenser and the liquid products were collected in a sampling bottle at 2 h intervals. Periodic gas sampling was also performed every 2 h using Tedlar sampling bags. The collected liquid products were centrifuged for 1 h to separate the aqueous fraction (AF) and organic fraction (OF). The experiments were performed over a period of 4 h. Table 2.1 describes the numbered components of the continuous packed-bed reactor provided in Figure 2.1, Figure 2.2a and Figure 2.2b. Figure 2.2. shows the method of catalyst loading in the continuous packed-bed reactor (a. Method of catalyst loading inside the reactor, enclosed in a furnace; b. Inside reactor with loaded catalyst).

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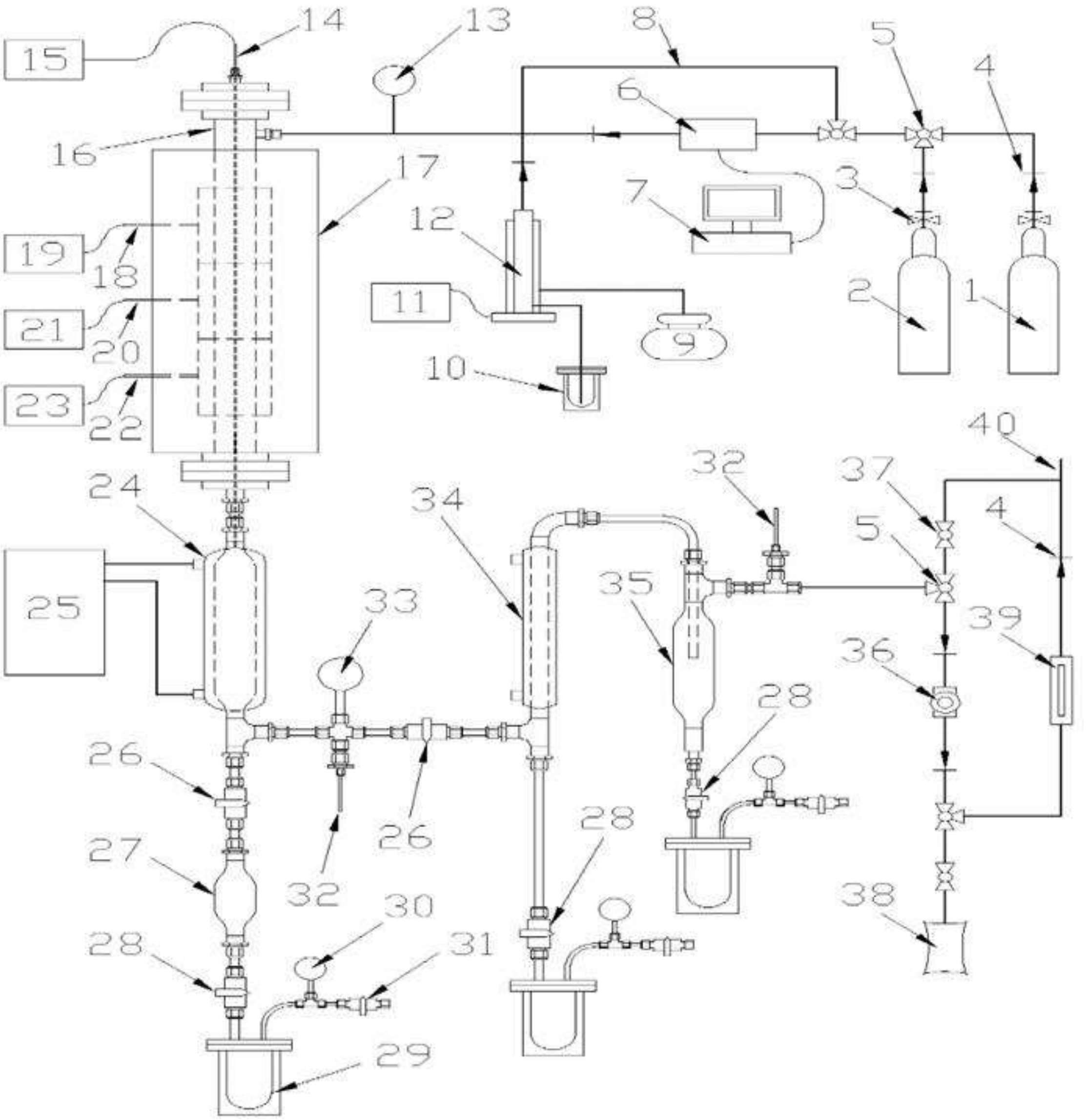

Figure 2.1 Schematic of the continuous packed-bed reactor.

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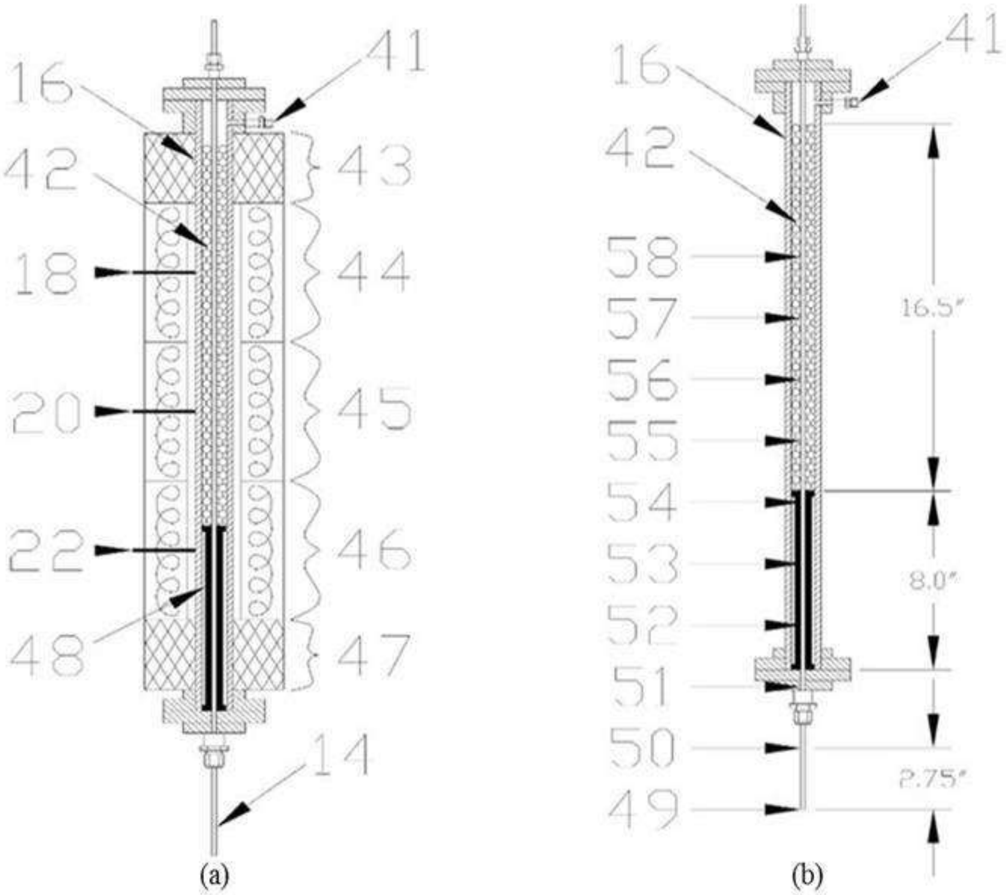

Figure 2.2 Method of catalyst loading in continuous packed-bed reactor

(a. Method of catalyst loading inside the reactor, enclosed in a furnace; b. Inside reactor with loaded catalyst).

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Table 2.1 The numbered components of the continuous packed-bed reactor.

1	Hydrogen cylinder	30	Sampling vessel pressure gauge
2	Air cylinder	31	Sampling vessel ball valve
3	Cylinder regulator	32	Thermocouple
4	Check valve	33	Reactor exit pressure gauge
5	Three-way valve	34	Condenser 2
6	Mass flow controller (MFC)	35	Condenser 3
7	Computer-MFC program	36	Back pressure regulator
8	MFC bypass line	37	Needle valve
9	Air compressor	38	Gas sample bag
10	Bio-oil	39	Exit gas flow meter
11	High pressure pump controller	40	Gas exit line
12	High pressure pump	41	Bio-oil inlet
13	Reactor inlet pressure gauge	42	Catalyst
14	Ten zone reactor thermocouple	43	Heater top insulation, 3” long
15	Ten zone thermocouple monitor	44	Heater zone 1, 6” long
16	Reactor tube	45	Heater zone 2, 6” long
17	Reactor tube heater	46	Heater zone 3, 6” long
18	Heater zone 1 thermocouple	47	Heater bottom insulation, 3” long
19	Heater zone 1 controller	48	Catalyst support
20	Heater zone 2 thermocouple	49	Reactor thermocouple zone 1
21	Heater zone 2 controller	50	Reactor thermocouple zone 2
22	Heater zone 3 thermocouple	51	Reactor thermocouple zone 3
23	Heater zone 3 controller	52	Reactor thermocouple zone 4
24	Condenser 1	53	Reactor thermocouple zone 5
25	Chiller	54	Reactor thermocouple zone 6
26	Ball valve	55	Reactor thermocouple zone 7
27	Hydrocarbons storage vessel	56	Reactor thermocouple zone 8
28	Needle valve	57	Reactor thermocouple zone 9
29	Sampling vessel	58	Reactor thermocouple zone 10

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2.4 Physical and chemical analysis

Raw bio-oil (RBO) and the HCF produced from the hydroprocessing treatments were characterized following ASTM methods. For the AV test, 1 g of sample was dissolved in isopropanol/water (v/v =35:65) solution and then titrated with 0.1 N NaOH to a pH of 8.5. The AV was then calculated as the required milligrams (mg) amounts of NaOH equivalent to 1 g of sample, according to ASTM D664. The HHV was determined with a Parr 6400 automatic isoperibol calorimeter according to ASTM D240. The Karl Fischer method was employed to determine water content by ASTM E203 with a Cole-Parmer Model C-25800-10 titration apparatus. Elemental analysis (CHNO) for determination of percent carbon (C), percent hydrogen (H), percent nitrogen (N) and percent oxygen (O) were determined by EAI CE-440 elemental analyzer, with oxygen content determined by difference by the ASTM D5291 method. Based on the significantly superior peformance of the catalyst, one best-performing catalyst (based on properties and yields) will be chosen for more detailed analysis. Product analysis was by detailed hydrocarbon analysis (DHA) and simulated distillation (SIMDIS). DHA was performed by a PerkinElmer Clarus 680 GC equipped with a built-in model Arnel 4060 DHA analyzer, performed by ASTM D6730-01 method. SIMDIS was performed by the ASTM D2887 method on a gas chromatograph, gas chromatography mass spectroscopy (GC-MS) and Fourier transform infrared spectroscopy (FTIR).

2.5 Experimental design

Each experiment was performed following 3 replicates. A factorial arrangement of treatments in a completely randomized design was employed with the one factorial being catalyst type. The statistical analysis was performed with SAS software version 9.3.

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The analysis of variance (ANOVA) model as shown in Eq. 2.2 was comprised of one factorial with six catalyst levels, four reduced and two sulfided catalysts (Ni/Si-Al, NiW/Si-Al, FeW/Si-Al, CoMo/γ-Al_2O_3, sulfided (CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3) catalysts to determine their influence on physical properties of AV, HHV, oxygen content and WC. ANOVA Eq. 2.2 was also applied to yield analysis. The ANOVA results showed that the main effect of catalyst type treatments were significant at the 0.05 level of significance for all physical properties as well as yields, satisfying the requirement of Fisher's protected LSD (Steel et al. 1980). The least significant difference (LSD) test was performed to separate the physical property means as influenced by the catalyst treatments.

The ANOVA model was performed for each of the physical properties and liquid yields.

$$Y_i = \beta_0 + \beta_1 A_i + e_i \qquad \text{Eq. 2.2}$$

Where:

Y_i represents dependent variable physical or chemical testing values: acid value, HHV, Oxygen percent, WC and yields,

β_0 represents the intercept term,

$\beta_1 A_i$ represents the influence of catalyst type ((Ni/Si-Al, NiW/Si-Al, FeW/Si-Al, CoMo/γ-Al_2O_3, sulfided CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3)

e_i represents random error term.

The efficacy of catalyst treatment means were compared by the LSD comparison of means method performed for each of the physical properties (AV, HHV, WC, oxygen content); yields (total yields (TY, AF and OF) were also independently tested by the LSD

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method. The 3 replicate values of each catalytic treatment were included in the test to determine the influence of each catalyst on properties and yields. Following Fisher's protected LSD test for ANOVA significance multiple comparison of means were performed by LSD for each physical property (AV, HHV, WC, oxygen content). Yields were also tested in an ANOVA with Fisher's protected LSD test performed to determine significance. The OF yields were then compared by an LSD multiple comparison of means test.

2.6 Results and Discussion

2.6.1 Catalyst Screening

Table 2.2 gives the mean values of the AV, HHV, Oxygen percent and WC and yields to analyze the effect of catalyst type treatments (Ni/Si-Al, NiW/Si-Al, FeW/Si-Al, CoMo/γ-Al_2O_3 and sulfided CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3). Each experiment was repeated 3 times to perform statistical analysis. Letters in parentheses indicate significant differences between property means as influenced by catalyst type.+

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Table 2.2 Effect of catalyst on mean values[1] for physical properties.

Catalyst	AV (mg KOH/g)	HHV (MJ/Kg)	Oxygen content (%)	WC (%)
Rawbio-oil (Control)	95.9 (a)	16.4 (g)	54.7 (a)	29.2 (a)
Ni/Si-Al	44.7 (c)	35.9 (d)	14.2 (d)	5.1 (b)
NiW/Si-Al	45.8 (b)	33.5 (f)	18.6 (b)	5.1 (b)
FeW/Si-Al	42.4 (d)	34.6 (e)	15.9 (c)	4.6 (c)
Reduced CoMo/γ-Al_2O_3	18.8 (e)	37.9 (c)	11.5 (e)	4.0 (d)
Sulfided CoMo/γ-Al_2O_3	5.2 (g)	41.2 (a)	4.0 (g)	1.3 (f)
Sulfided NiMo/γ-Al_2O_3	9.4 (f)	39.4 (b)	7.0 (f)	2.0 (e)

(AV, HHV, Oxygen content (%), WC (%). Letters in parentheses indicate significant differences between property means as influenced by catalyst type.

[1] Different letters to the right of the physical property (AV, HHV, oxygen content, WC %) indicate any significant difference between treatments.

The mean AV for reduced catalysts of Ni/Si-Al, NiW/Si-Al, FeW/Si-Al and CoMo/γ-Al_2O_3 decreased significantly from 95.9 to 44.7, 45.8, 42.4 and 18.8 mg KOH/g respectively. Among the reduced catalysts, CoMo/γ-Al_2O_3 AV was significantly lower than the other three reduced catalysts. These values are all approximately half of the AV of raw bio-oil. For the sulfided CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3 the mean AV decreased significantly from 95.9 to 5.2 and 9.4 mg KOH/g respectively. Among all tested catalysts (both reduced and sulfded catalysts), sulfided CoMo/γ-Al_2O_3 had the significantly lowest AV of 5.2 mg KOH/g.

The mean HHV of reduced catalysts for Ni/Si-Al, NiW/Si-Al, FeW/Si-Al and CoMo/γ-Al_2O_3 were increased from 16.4 to 35.9, 33.5, 34.6 and 37.9 MJ/Kg respectively, the increase was more than double the HHV of raw bio-oil. The HHV's of Ni/Si-Al, NiW/Si-Al and FeW/Si-Al differed very little with each other. Among the reduced catalysts the CoMo/γ-Al_2O_3 HHV was significantly higher than the other three reduced catalysts. In the case of the sulfided catalysts, the sulfided CoMo/γ-Al_2O_3 and NiMo/γ-

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Al_2O_3 had mean HHV's of 41.2 and 39.4 MJ/Kg respectively, which were significantly higher than the HHV of the control (16.4 MJ/Kg) and the other four reduced catalysts HHV (35.9, 33.5, 34.6 and 37.9 MJ/Kg). From the tested catalysts, sulfided CoMo/γ-Al_2O_3 catalyst showed the highest HHV of 41.2 MJ/Kg, followed by NiMo/γ-Al_2O_3 with the second highest HHV of 39.4 MJ/Kg.

The mean oxygen content for reduced catalysts of Ni/Si-Al, NiW/Si-Al, FeW/Si-Al and CoMo/γ-Al_2O_3 was decreased significantly from 54.7 to, 14.2, 18.6, 15.9 and 11.5% respectively. Among the reduced catalysts CoMo/γ-Al_2O_3 performed the best in terms of oxygen content. For the sulfided catalysts CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3 showed an oxygen content reduction from 54.7 to 4.0 and 7.0 % respectively. The OF of the product obtained with sulfided CoMo/γ-Al_2O_3 catalyst had significantly lower mean oxygen content followed by NiMo/γ-Al_2O_3 catalyst with the next lowest oxygen content (7.0%).

The mean WC percentages for Ni/Si-Al, NiW/Si-Al, FeW/Si-Al and CoMo/γ-Al_2O_3 catalysts were decreased from 29.2 to 5.1, 5.1, 4.6 and 4.0% respectively. The statistical results show that, the WC content of the OF did not differ significantly between the Ni/Si-Al and NiW/Si-Al catalysts. The sulfided catalysts CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3, had the WC percentage values of 1.3 and 2.0 in comparison to the control, which had a WC of 29.2%. The WC percentage for the sulfided catalysts CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3 differed a little (0.7% difference), but the difference was significant statistically. A comparison of results for both the reduced and sulfided catalysts showed sulfided CoMo/γ-Al_2O_3 had significantly superior performance in terms of reduction.

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The yields, overall yields (TY), AF and OF, for hydroprocessing treatments are given in Table 2.3, with different letters given in brackets indicating a significant difference between each catalyst treatment mean.

Table 2.3 Effect of catalysts on yields (TY, aqueous (AF) and organic fraction (OF)).

Catalyst	TY (wt%)	AF (wt%) yield	OF (wt%) yield
Ni/Si-Al	67.1 (d)	51.4 (f)	16.3 (d)
NiW/Si-Al	66.6 (e)	57.0 (e)	9.7 (f)
FeW/Si-Al	67.1 (d)	52.9 (d)	14.3 (e)
Reduced CoMo/γ-Al_2O_3	68.4 (c)	53.1 (c)	15.7 (c)
Sulfided CoMo/γ-Al_2O_3	85.3 (b)	58.2 (b)	27.0 (a)
Sulfided NiMo/γ-Al_2O_3	86.3 (a)	61.5 (a)	25.1 (b)

The mean TY yields for Ni/Si-Al, NiW/Si-Al, FeW/Si-Al and CoMo/γ-Al_2O_3 were 67.1, 66.6, 67.1 and 68.4% respectively. The mean TY yields of Ni/Si-Al and FeW/Si-Al did not differ significantly. For the sulfided catalysts, CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3 the TY were 85.3 and 86.3% respectively. While the mean AF yields for Ni/Si-Al, NiW/Si-Al, were 51.4 and 57.0% and differed significantly from the mean AF of FeW/Si-Al (52.9%) and CoMo/γ-Al_2O_3 (53.1%) respectively. For sulfided catalysts the mean AF yields were 58.2 and 61.5% respectively. Among all the catalysts reduced FeW/Si-Al and CoMo/γ-Al_2O_3 had the significantly lowest AF yields. For reduced catalysts, Ni/Si-Al, NiW/Si-Al, FeW/Si-Al and CoMo/γ-Al_2O_3 the mean OF yields were 16.3, 9.7, 14.3, and 15.7%, respectively, and each mean differed significantly. For the sulfided catalysts, CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3, the OF yields were 27.0 and 25.1%, respectively, with these means differing significantly.

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The sulfided catalysts, CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3, had the significantly highest OF yields among the catalyst treatments tested. The sulfided CoMo/γ-Al_2O_3 catalyst had the significantly highest OF yields. Though the TY yields (86.3%) for sulfided NiMo/γ-Al_2O_3 was significantly the highest, it yielded a product with high AF (61.5%) in comparison to sulfided CoMo/γ-Al_2O_3 (58.3%). For best performing sulfided CoMo/γ-Al_2O_3 catalyst, gas yields and char yields were calculated as shown in below Table 2.4. The organic fraction (OF), aqueous (AF), gas and char yields were 27.0, 58.2, 8.7 and 6 to 8.0 wt% respectively.

Table 2.4 Yields OF, AF, gas and char yields for sulfided CoMo/γ-Al_2O_3 catalyst.

Yields	wt%
OF	27.0
AF	58.2
Gas	8.7
Char	6 to 8.0

Based on the results of OF yields and oxygen content we have determined that the sulfided CoMo/γ-Al_2O_3 catalyst had the significantly highest OF yield and lowest oxygen content. In terms of the remaining physical and chemical test results we observed that the sulfided CoMo/γ-Al_2O_3 catalyst had the lowest AV, highest HHV, and lowest WC percentage. Therefore, the sulfided CoMo/γ-Al_2O_3 catalyst performed the best. The high activity of sulfided CoMo/γ-Al_2O_3 catalyst was due to the formation of Co-Mo-S phase in the catalyst. Co-Mo-S phase is believed to be the active phase, and is formed by the intercalation of Co at the edges of MoS_2 surface. Based on the significantly superior

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peformance of the sulfided CoMo/γ-Al_2O_3 catalyst, it was chosen for more detailed analysis.

Table 2.5 shows the analysis of gas samples collected during the hydroprocessing experiments for sulfided CoMo/γ-Al_2O_3 catalyst. Gas samples were collected prior to collecting the liquid samples. Gas analysis was used to interpret the exit gases. The exit gases from the experiment using sulfided CoMo/γ-Al_2O_3 catalyst had 65.5% hydrogen, 0.2% oxygen, 0.5% nitrogen, 3.1% methane, 0.15% carbon monoxide, 8.1% carbon dioxide and 22.4% methane, respectively.

Table 2.5 Gas analysis, hydrogen consumption and the hydrogen conversion for the hydroprocessed product (OF) of the sulfided CoMo/γ-Al_2O_3 catalyst.

Gas	Units
H	65.60%
O	0.20%
N	0.50%
CH_4	3.10%
CO	0.10%
CO_2	8.10%
C_2H_4	22.80%
Hydrogen consumption	203.2 ml/min
Hydrogen conversion	79.70%
Yields on dry basis (g/g feed)	g/g feed
Gas yield	0.08
AF yield	1.0
OF Yield	0.39

The exit gases from the experiment using sulfided CoMo/γ-Al_2O_3 catalyst had 65.5% hydrogen, 0.2% oxygen, 0.5% nitrogen, 3.1% methane, 0.15% carbonmonoxide, 8.1% carbon_dioxide and 22.4% methane respectively. The hydrogen consumption and

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hydrogen conversion for sulfided CoMo/γ-Al_2O_3 was 79.7% and 203.2 ml/min. Higher hydrogen consumption indicates higher deoxygenation.

Yields of hydroprocessed product including gas, AF and OF from the experiment using sulfided CoMo/γ-Al_2O_3 catalyst based on dry basis (g/g feed) were 0.08, 1.0 and 0.39 g/g feed respectively.

2.7 Analysis

2.7.1 DHA Analysis

Figure 2.3 shows the DHA of mixed liquid hydrocarbons obtained with sulfided CoMo/γ-Al_2O_3 catalyst, perfomed according to ASTM D6730-01. Antiknock rating of the OF (fuel mixture) was expressed by octane number, and determined by gas-chromatographic method based on the hypothesis that to each individual gasoline component corresponds a particular effective octane factor. The effective octane number of a gasoline as a mixture is determined by summing up the derivatives of the mass proportion of individual components into their effective octane factors. For example, to simplify the calculation procedure, the chromatogram is divided in to groups (for example 31) as given in below equation Eq. 2.3.

$$q = {}^{31}\sum_{i=1} W_i q_i \qquad \text{Eq. 2.3}$$

Where q is the octane number of the gasoline, W is the mass proportion of the *i*-th octane group of the gasoline, and q is the effective octane number of the *i*-th componenets (Cherepista et al., 2001). The explanation for calculation of octane number will not be repeated again in other chapters.

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The DHA of the sulfided CoMo/γ-Al_2O_3 catalyst upgraded product predominately contained iso-paraffins, olefins, naphthenes and compounds greater than C14. The other compounds that are identified in minor amounts in comparison to iso-paraffins, olefins, naphthenes and compounds greater than C14 are aromatics and paraffins. The DHA analysis of the hydroprocessed product obtained with sulfided CoMo/γ-Al_2O_3 catalyst showed an octane value of 71.1.

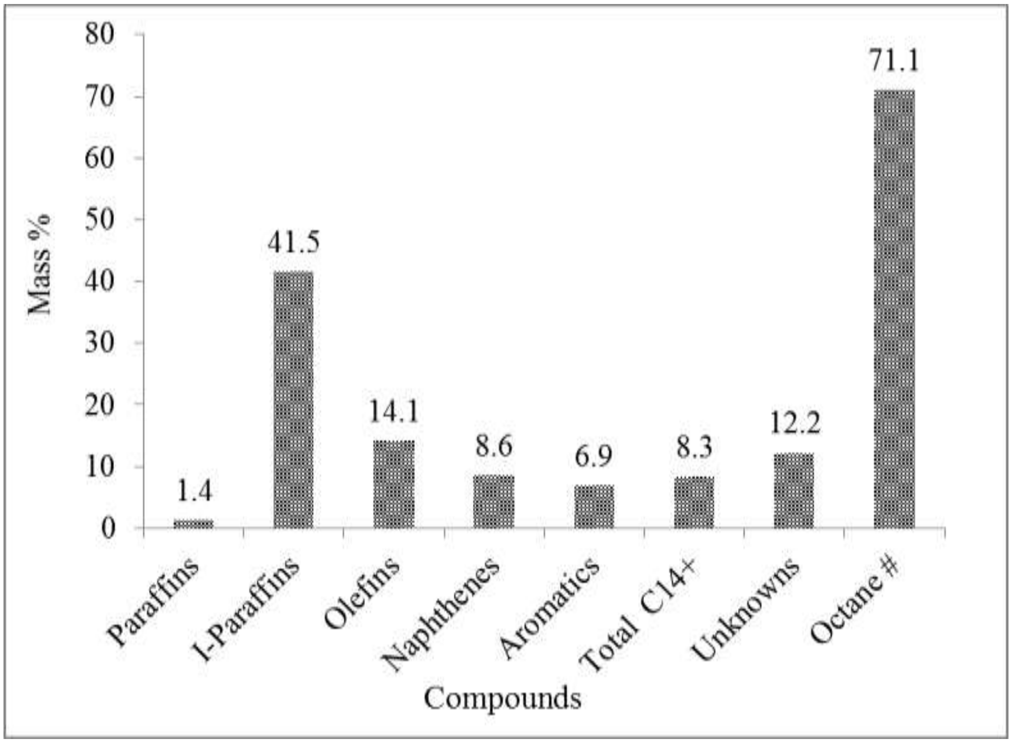

Figure 2.3 DHA of mass percentage (%) of OF's obtained from sulfided CoMo/γ-Al_2O_3 treatment.

2.7.2 SIMDIS

From the SIMDIS results (Figure 2.4), it can be reported that the OF produced by sulfided CoMo/γ-Al_2O_3 had a boiling temperature range of 156 to 355 °C, and contained

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petroleum equivalents of 85% gasoline (156 °C), 5% jet fuel (180-248 °C), and 5% diesel (248-306 °C) range hydrocarbons. SIMDIS also showed the presence of 5% vacuum gas oil (VGO) range (306- 355 °C) hydrocarbons in our fuel.

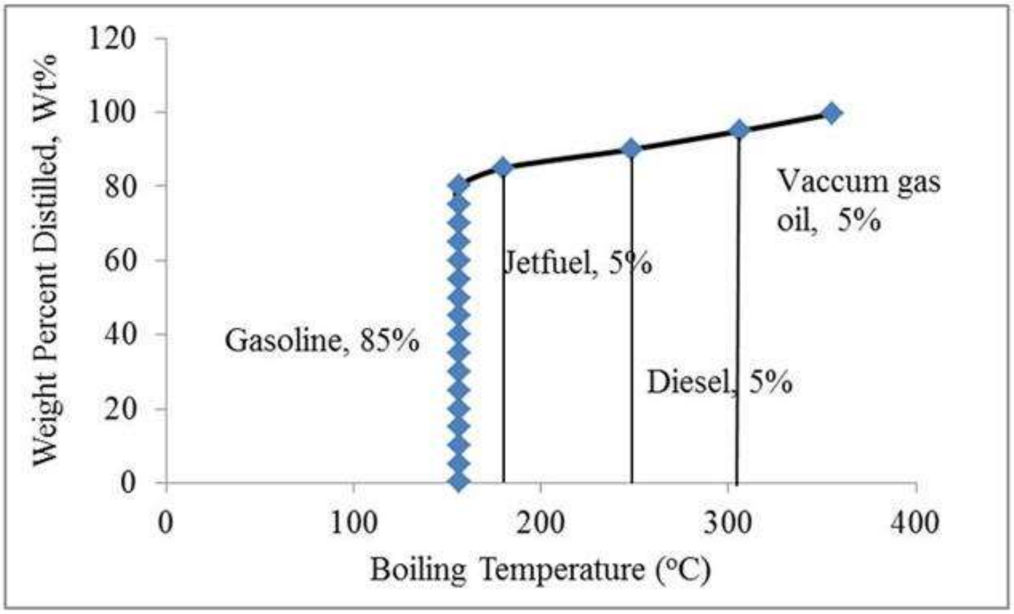

Figure 2.4 Wt% distilled vs boiling temperature (°C) of the sulfided CoMo/γ-Al_2O_3 upgraded liquid fuel determined by SIMDIS.

2.7.3 FTIR

FTIR spectral data was used to analyze the raw bio-oil and hydroprocessed product sample obtained with sulfided CoMo/γ-Al_2O_3 catalyst. Characteristic vibrational modes are observed at 3200-3600 cm^{-1} (OH stretching), 2850-2980 cm^{-1} (CH stretching, aliphatic), 1710 cm^{-1} (C=O stretching), 1375-1475 cm^{-1} (C–H vibrations) and 1100-1300 cm^{-1} (C-O stretching). From Figure 2.5, it was evident that after hydroprocessing, the OH stretching was decreased due to a decrease of oxygenated compounds such as carboxylic acids, water and alcohols present in raw bio-oil. The increase of C=O and C-O stretching

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peaks indicates the presence of oxygenated compounds in the bio-oil. The increase in intensity of 2850-2980 cm^{-1} (CH stretching, aliphatic) 1375-1475 cm^{-1} (C–H vibrations) and CH bending stretch were significantly increased. This change in the absorption band indicates that the carboxylic acids, aldehydes and other oxygenated compounds were converted into hydrocarbons. The FTIR spectral data shown in Figure 2.5 was in good agreement with the physical and chemical properties shown in Table 2.2.

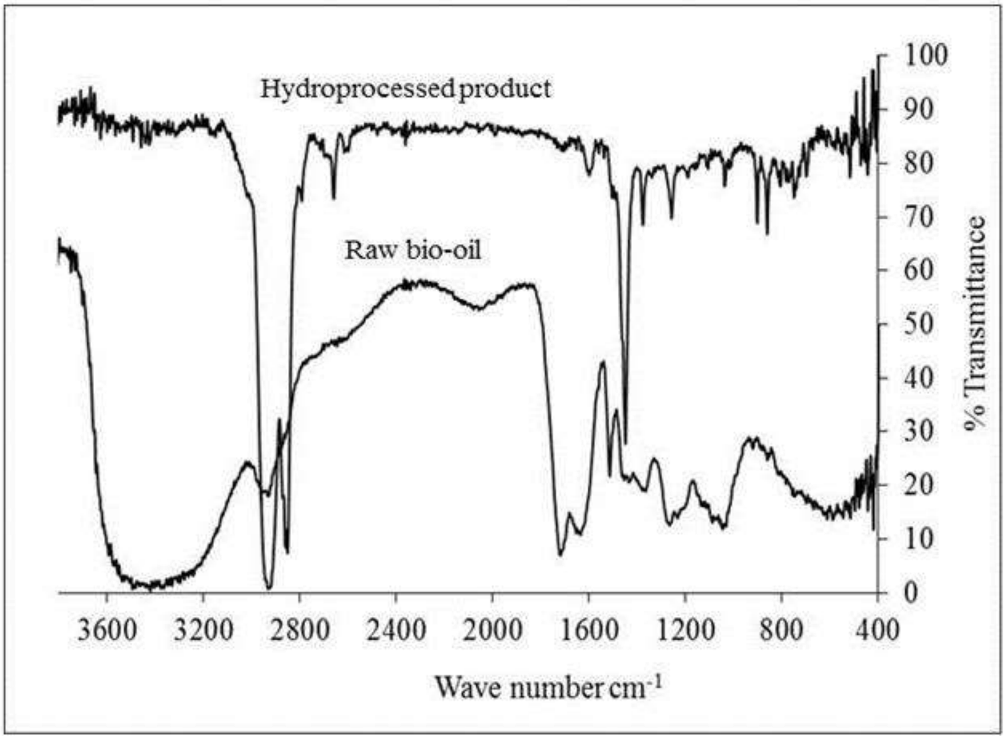

Figure 2.5 FTIR spectral comparison of raw bio-oil and hydroprocessed product obtained with sulfided CoMo/γ-Al_2O_3 catalyst.

2.7.4 Thermogravimetric Analysis (TGA)

TGA was performed on the used catalysts to determine the amount of residual carbon deposited on the catalyst surface. A Shimadzu instrument TGA-50 was used to

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perform the TG analysis. A required amount of catalyst was placed in an alumina pan and a temperature program was ramped up at a rate of 5 °C/min starting at room temperature and terminating at 800 °C. The runs were performed under air flow of 50 mL/min. The percentage weight loss of the fresh CoMo/γ-Al_2O_3, fresh sulfided CoMo/γ-Al_2O_3 and those of spent CoMo/γ-Al_2O_3 catalyst are shown in Figure 2.6, 2.7 and 2.8.

Figures 2.6, 2.7 and 2.8 show significant loss during the intial heating period at the temperature range between 100 to 220 ºC. This weight loss was due to the removal of moisture from the catalyst surface and also moisture from the interior of the pores. Part of the weight loss could also be due to the removal of easily oxidizable carbonaceous species formed during initial decomposition of the aromatic compounds. Further the water which was bound with the catalyst material requires higher temperature for desorption. In the case of TGA analysis of fresh CoMo/γ-Al_2O_3 (Figure 2.6) and fresh sulfided CoMo/γ-Al_2O_3 (Figure 2.7) no weight loss was observed due to carbon deposition. However, in the case of spent CoMo/γ-Al_2O_3 (Figure 2.8) catalyst weight loss of 2.8 mg was observed at a temperature between 300 to 535 °C, which indicates that there was only a slight carbon deposition on the surface of the catalyst.

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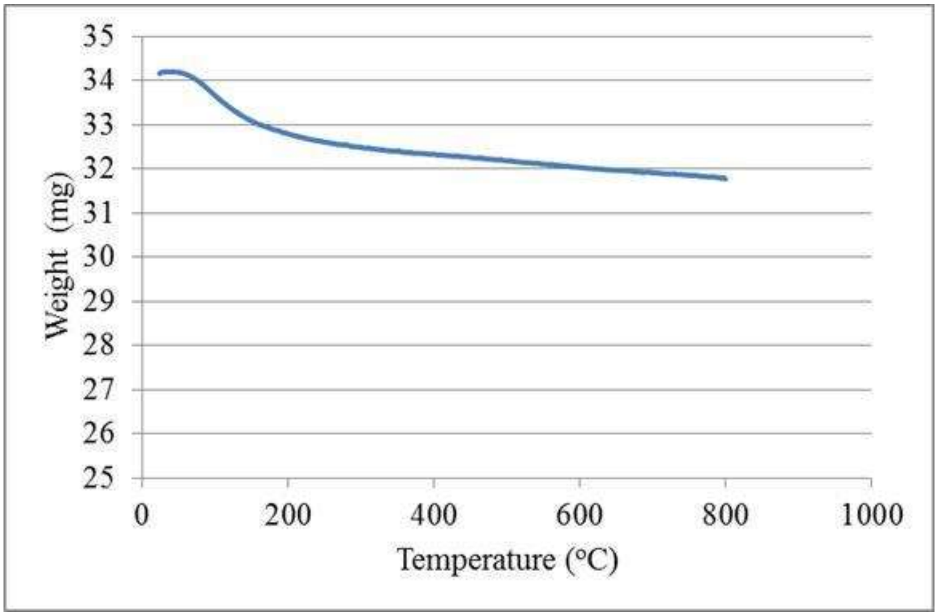

Figure 2.6 TGA of the fresh CoMo/γ-Al_2O_3 catalyst.

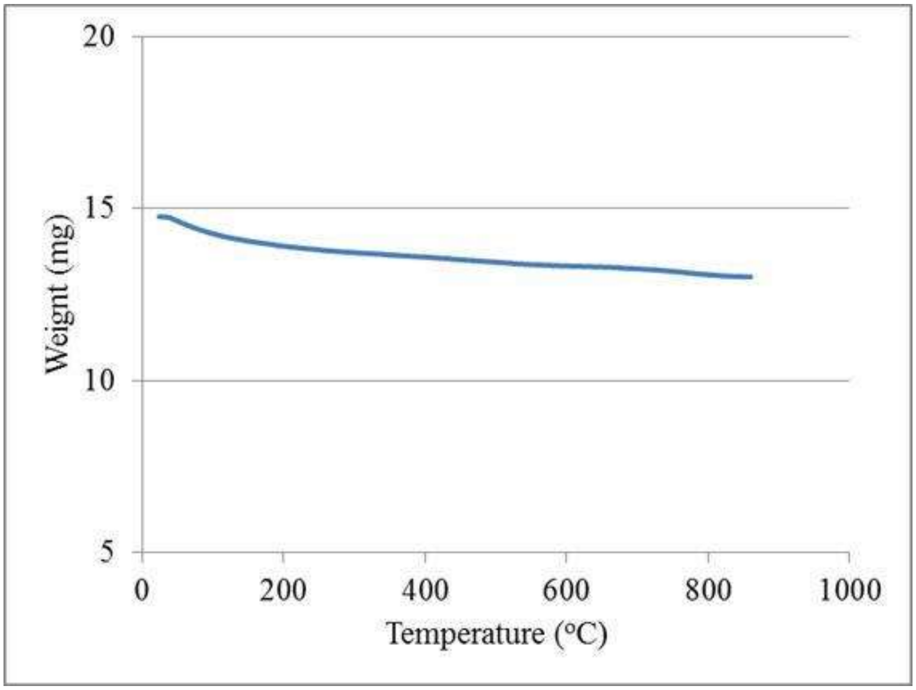

Figure 2.7 TGA of the fresh sulfided CoMo/γ-Al_2O_3 catalyst.

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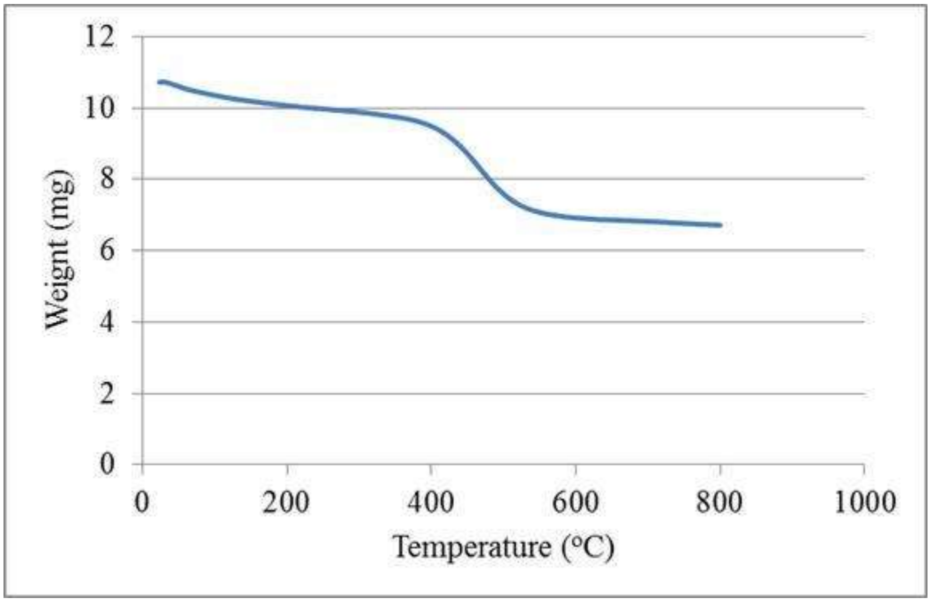

Figure 2.8 TGA of the used CoMo/γ-Al_2O_3 catalyst

2.8 Conclusion

Bio-oil has the potential to be utilized as a fuel. However, negative properties such as high acidity, high water content, high oxygen content, low energy density, corrosiveness, and thermal instability; have prevented its direct use as a fuel. In this study hydroprocessing of bio-oil was performed in a single-stage. The hydroprocessing experiments were performed in a continuous packed-bed reactor at a temperature range from 375 to 400 °C, 1000 psig hydrogen pressure, hydrogen flow rate of 500 ml/min and at a liquid hourly space velocity of 0.5 h^{-1} for a time period of 4 h. Six catalysts, four different reduced catalysts (Ni/Si-Al, CoMo/γ-Al_2O_3, NiW/Si-Al, FeW/Si-Al) and two sulfided catalysts (CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3) were tested. The activity of different catalysts was analyzed based on the physical and chemical properties, mainly AV, HHV, Oxygen percent and WC. The results were compared with the control and OF

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yields were also compared between catalysts. The ANOVA results indicated that the type of catalyst had a significant influence on the AV, HHV, WC, oxygen content and the OF yields.

Among the tested catalysts sulfided CoMo/γ-Al_2O_3 catalyst showed superior activity in terms of OF yield (27.0 wt%) and decreased oxygen content (4 wt%). Compared to raw bio-oil the hydroprocessed product produced by sulfided CoMo/γ-Al_2O_3 contained lower AV, oxygen content and WC and HHV of more than double value the value of the raw bio-oil. This was also further evident by the ANOVA statistical data analysis.

From FTIR, it was also evident that the increase in intensity of 2850-2980 cm^{-1} (CH stretching, aliphatic) 1375-1475 cm^{-1} (C–H vibrations) and CH bending stretch was significantly increased. This change in the absorption band indicates that the carboxylic acids, aldehydes and other oxygenated compounds were converted into hydrocarbons. The DHA of the sulfided CoMo/γ-Al_2O_3 catalyst upgraded product predominately contained iso-paraffins, olefins, naphthenes and compounds greater than C14. The other compounds that are identified in minor amounts in comparison to iso-paraffins, olefins, naphthenes and compounds greater than C14 are aromatics and paraffins. The DHA analysis of the hydroprocessed product obtained with sulfided CoMo/γ-Al_2O_3 catalyst showed an octane value of 71.1.

From the SIMDIS results it was reported that the OF produced by sulfided CoMo/γ-Al_2O_3 had a boiling temperature range of 156 to 355 ^{o}C, and contained petroleum equivalents of 85% gasoline (156 ^{o}C), 5% jet fuel (180-248 ^{o}C), and 5% diesel

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(248-306 ^oC) range hydrocarbons. SIMDIS also showed the presence of 5% vacuum gas oil (VGO) range (306- 355 ^oC) hydrocarbons in the fuel.

TGA analysis showed only slight (2.8 mg) coke deposition on the catalyst surface in comparison to fresh sulfided CoMo/γ-Al_2O_3 catalyst.The higher activity of the catalyst was due to the formation of Co-Mo-S phase in the catalyst. Co-Mo-S phase is believed to be the active phase, and is formed by the intercalation of Co at the edges of MoS_2 surface.

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CHAPTER III

EFFECT OF PROCESS CONDITIONS ON SINGLE-STAGE HYDROPROCESSING OF BIO-OIL IN A CONTINUOUS PACKED-BED REACTOR

3.1 Abstract

Hydroprocessing (hydrotreating and hydrocracking) of raw bio-oil was performed in a continuous packed-bed reactor utilizing sulfided CoMo/γ-Al_2O_3 catalyst. Process conditions were varied to determine the most effective temperature (325-350, 375-400, 400-425°C), hydrogen pressure (1000, 1500 psig), hydrogen flow rate (500, 1000ml/min) and liquid hourly space velocity (0.1, 0.3, 0.7, 1 h^{-1}). The most effective process conditions for the sulfided CoMo/γ-Al_2O_3 catalyst were for a temperature of 375-400 °C, pressure of 1500 psig, liquid hourly space velocity of 0.3 h^{-1} and hydrogen flow rate of 1000 ml/min. These conditions produced both higher yields and satisfactory properties.The product properties of the hydroprocessed raw bio-oil for the best combination of treatment conditions were an acid value of 0.7 mg of KOH/g, higher heating value of 44.01 MJ/kg, percentage water content of 0.1%. The elemental carbon, hydrogen, nitrogen and oxygen properties were 87.0, 13.0, 0.3 and 0.1%, respectively. The total liquid yields, organic fraction and aqueous fraction were 85.1, 24.6 and 60.6%, respectively. The organic fraction was also analyzed by detailed hydrocarbon analysis, GC-MS and FTIR analysis.

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3.2 Introduction

Bio-oil derived from fast pyrolysis of biomass has the potential to serve as substitute for petroleum in the transportation fuel sector. However, bio-oil has deleterious properties such as high viscosity, water content, corrosiveness, low heating value and low stability (Czernik and Bridwater 2004). Therefore, bio-oil must be upgraded before its utilization in gasoline and diesel engines. Pyrolysis bio-oil is a complex mixture of oxygenates with more than 300 different compounds identified (Czernik and Bridgwater 2004). Typical bio-oils contain water (20-30 wt%), lignin fragments (15-30 wt%), aldehydes (10-20 wt%), carboxylic acids (10-15 wt%), carbohydrates (5-10 wt%), phenols (2-5 wt%), furfurals (1-4 wt%), alcohols (2-5 wt%) and ketones (1-5 wt%) (Bridgwater 2002).

The undesirable properties of bio-oil are due to its high oxygen content. Current upgrading techniques include catalytic hydroprocessing (Elliot 2007), esterification (Tang et al., 2008, Xu et al., 2010, Xiong et al., 2009), olefination (Zhang et al., 2011, Zhang et al., 2013, Chatterjee et al., 2013), catalytic pyrolysis (French et al., 2010, Aho et al., 2007), hydrodeoxygenation (HDO) (Elliot 2007, Wildschut et al., 2009, Senol et al. 2005), steam reforming (Wang et al., 1996, Galdamez et al., 2005), decarbonylation and decarboxylation (Mortensen et al., 2011). Hydrodeoxygenation (HDO) has been studied extensively for conversion of bio-oil to liquid hydrocarbons. A variety of catalysts, have been applied for the HDO of bio-oil including conventional catalysts for petroleum hydroprocessing and noble metal catalysts such as Rh, Pt, Pd/ZrO_2 (Ardiyanti et al., 2011) and Ru/Al_2O_3, Ru/C, Ru/TiO_2, Pd/C and Pt/C (Wildschut et al., 2009, Wildschut et al., 2010).

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Several studies have been reported on oxygen removal from oxygenated model compounds with catalysts other than conventional sulfided catalysts (Zhang et al., 2006, Snare et al., 2006, Kubickova et al., 2005, Shin et al., 2000, Mahata et al., 1999). Sulfided catalysts are commonly utilized in refineries for hydrotreatment in the presence of hydrogen to remove heteroatoms, such as sulfur, nitrogen, oxygen and metals, from crude oil (Czernik et al., 2002, Topsøe et al., 1996).

Thus, hydrodesulfurisation (HDS), hydrodenitrogenation (HDN), HDO and hydrodemetallation (HDM) as well as hydrogenation reactions take place simultaneously during hydrotreating of crude oil (Furimsky et al., 2000, Topsøe et al., 1996).

The conventional HDS and HDN CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3 catalysts have been the most commonly applied catalysts in HDO studies. In these catalysts Mo serves as an active element while Co or Ni as a promoter supported on γ-Al_2O_3 or without support (Furimsky et al., 2000, Topsøe et al., 1996, Senol et al., 2007, Senol et al., 2005, Senol et al., 2007, Senol et al., 2007, Senol et al., 2005, Yoosuk et al., 2012). The concentration of the active metals on the support usually varies from 8 to 25 wt% and the promoter percentage varies from 1 to 4 wt%.

The CoMo and NiMo catalysts are more active in the sulfided form than in the non-sulfided form. Therefore, the catalysts are either presulfided with a sulfiding agent or sulfided on stream by the addition of a sulfiding agent to the feed. The sulfiding agent can be either hydrogen sulfide or a carbon containing sulfur compound (Senol 2007). The relatively higher activity of sulfided CoMo or NiMo/γ-Al_2O_3 can be attributed to the formation of the active Co(Ni)MoS phase, consisting of highly dispersed MoS_2 crystallites coated with Co or Ni atoms that act as promoters when the oxide form is

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subjected to the sulfidation process (Nikulshin et al., 2014). Sulfidation changes the surface structure of the catalyst, and creates active sites with various configurational and energetic properties. It is generally agreed that sulfur anion vacancies (coordinatively unsaturated sites), located at the edge of MoS_2 nanoclusters are the catalytic sites formed in the presence of a sulfiding agent and hydrogen. These sites show Lewis acid character, and they can adsorb atoms with unpaired electrons. Thus, the sulfur anion vacancies can play a role in the scission of carbon-heteroatom bonds (Senol 2007).

The promoter Ni and Co atoms occupy the edge of MoS_2 phases forming the Co-Mo-S and Ni-Mo-S structures at the interface (Brorson et al., 2007) which through d-electron donation causes the Mo to mimic a noble metal catalytic material (Chianell et al., 2009). Additives such as P (Yang et al., 2009), K (Centeno et al., 1995) or Pt (Centeno et al., 1995) were added to CoMoS or NiMoS catalysts for HDO.

Sulfur anion vacancies associated with the promoter atom have been discovered to be more active than those associated with the Mo atom. The surface of the catalysts consists of S^{2-}, H^+ and SH^- groups. H^+ and SH^- groups show Bronsted acid character, and they provide hydrogen for hydroprocessing reactions with regard to application as bio-oil HDO catalysts.

The sulfided CoMo and NiMo catalysts have been tested by previous researchers at a wide range of operating conditions, reactor types and feedstocks. Pacific Northwest National Laboratory (PNNL) researchers initially performed tests on liquefaction products rather than on fast pyrolysis bio-oil and screened 22 catalysts to determine their potential for HDO. The researchers selected CoMo 0402/S, HT 400/S and Ni-1404 as the most promising hydrotreating catalysts for further testing. The nickel catalyst showed

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performance similar to that of sulfided CoMo catalyst, but it produced high gas yields and consumed a high amount of hydrogen. Researchers also observed that the catalytic activity of the nickel catalyst was lost after several hours of testing (Elliott 2007).

PNNL researchers performed further studies with HT 400/S catalyst to compare its performance on a liquefied bio-oil containing primarily cyclic ketones and single-ring phenolics and a second liquefied bio-oil containing primarily multi-ring phenolics at a temperature of 398 °C and 13.8 Mpa of pressure. In these tests researchers obtained a light hydrocarbon product from the first liquefied bio-oil, but in the case of the second liquefied bio-oil, the alkaline content of the oil deposited on the catalyst over a 48 h. HDO test resulted in deactivation of the catalyst and reactor blockage. Based on these results researchers hypothesized that a two-stage process may reduce bio-oil polymerization that cause the tar formation and subsequent catalyst coking (Elliott 2007).

PNNL also tested a new HDO catalyst CoMo/γ-Al_2O_3 that is reported in a 1993 patent (Baker and Elliot 1993) utilizing a two-stage hydroprocessing treatment based on their earlier hypothesis cited above. An intial hydrotreating 1st-stage process was employed at mild temperature conditions of 180 to 240 °C and a 2nd-stage hydrocracking treatment was then employed at temperatures of 300 to 400 °C. This two-stage process eliminated problems of early polymerization of the bio-oil and the reactor blockage previously experienced (Elliott 2007). This was achieved by the 1st-stage process partially hydrotreating the bio-oil to reduce water and oxygen content and producing some hydrocarbon content in the hydrotreated product. This partial upgrading allowed a 2nd-stage treatment to be applied at higher temperature without bio-oil polymerization, or rapid catalyst coking resulting in reactor blockage. This 2nd-stage treatment has become

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the standard method practiced by nearly all researchers since the Baker and Elliot (1993) discovery.

Elliot (2007) also reported on catalytic hydrotreatment performed by Veba Oel AG. Veba Oel AG performed a single-stage HDO treatment at temperatures below 300 ^{o}C. Tests were performed in a continuous feed bench-scale reactor at 17.8 MPa of pressure and temperatures of 350 to 370 ^{o}C over sulfided CoMo and NiMo catalysts. In this process researchers obtained bio-oil yields ranging from 30 to 35% with deoxgenation rates ranging from 88.0 to 99.9%. However, in this process the catalyst was deactivated relatively quickly and the formation of gum-like deposits blocked the reactor. It was also evident, that the application of a single-stage HDO treatment was not a viable approach for CoMo and NiMo catalysts.

Elliott et al. (2009) describes PNNL research in which both hydrotreatment and hydrocracking were combined within the same hydroprocessing reactor with two levels of temperature maintained in the catalyst bed, so that both the hydrotreating and hydrocracking steps were performed without separation of intermediate products to prevent loss and treatment cost of the material. In this process bio-oil from four feedstocks were consecutively hydrotreated and hydrocracked with Pd/ C catalyst. Hydrotreating was applied at a temperature range of 340 to 370 ^{o}C for 35 h, and hydrocracking was performed at 400 ^{o}C. Researchers observed no coke formation. However, with the later application of a higher flow rate performed between 30 to 40 h at 340 ^{o}C the hydroprocessing reactor plugged. The researchers hypothesized that when both hydrotreatment and hydrocracking were combined at appropriate temperatures within the same hydroprocessing reactor the carbon loss in the byproduct water stream

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was minimized. They concluded that a low flow rate was needed to result in successful production of hydrocarbons.

Elliott et al. (2012) reported on two-stage catalytic hydroprocessing of pine fast pyrolysis oil in a bench scale continuous-flow fixed-bed catalytic reactor system to evaluate the performance of fully sulfided catalyst beds including both ruthenium and promoted molybdenum. A two-stage treatment was employed at a temperature of approximately 170 ^{o}C and at an LHSV of 0.19 with sulfided Ru/C catalyst. This was followed by a second-stage hydrocracking treatment at a temperature of 400 ^{o}C for the same LHSV with both sulfided CoMo or NiMo. The HDO was operated for 90 to 99 h depending on the catalyst type. The hydroprocessed product had densities of 0.82 to 0.92 g/ml, oxygen content ranging from 0.2 to 2.7 wt %, and total acid value ranged from 0.01 to 2.7 mg KOH/g. However, catalyst bed plugging and pressure drop increase resulted from char particles plugging the catalyst bed. Researchers concluded that pre-filtration of bio-oil will be required for fixed-bed hydroprocessing to assist in preventing reactor plugging.

Sheu et al. (1988) pyrolyzed bio-oil produced from southern pine sawdust and bark was hydrotreated in a tricke-bed reactor system. The researchers utilized $Pt/Al_2O_3/SiO_2$ and the sulfided catalysts, $CoMo/\gamma\text{-}Al_2O_3$, $Ni\text{-}W/\gamma\text{-}Al_2O_3$ and $NiMo/\gamma\text{-}Al_2O_3$, tested at temperatures ranging from 623 to 673 K, with pressures varying from 750 to 1500 psig and with a varied WHSV of 0.5 to 3.0 h^{-1}. They concluded that the NiMo catalyst was superior with respect to product oil yield and stability of the catalyst in comparison to the others tested.

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Zhang et al. (2003) performed the HDO of fast pyrolysis bio-oil in the presence of CoMo/γ-Al_2O_3 catalyst. Effects of reaction time, temperature, and partial hydrogen pressure were determined. Experiments were performed in a 500 mL batch reactor at 360, 375, and 390 °C in tetralin. Researchers concluded that, as reaction time increased, the deoxygenation rate increased. However, after 20 min the deoxygenation rate decreased due to deactivation of the catalyst. They also concluded that hydrogen pressure had little effect on the deoxygenation of bio-oil. The oxygen content decreased from 30 wt% to 5 wt%. Full deoxygenation of bio-oil was not achieved in these experiments.

Two-step processing has been shown to improve bio-oil hydroprocessing results. A low temperature hydrotreatment enables stabilization through reactions like olefin, carbonyl and carboxylic groups reduction while a further high temperature hydrotreatment aims at hydrodeoxygenation of phenols and hydrocracking of larger molecules. The tests demonstrated that a temperature ranging between 350 and 450 °C would be required for full hydrorefining of pyrolysis oils and for the elimination of phenolic and furanic oxygenates and for the conversion of heavy molecules (Grange 1996).

With regard to other HDO operating conditions, a pressure ranging from 75 to 300 bar has been reported by researchers (Venderbosch et al., 2010, Mercarder et al., 2010, Elliot et al., 2009). An operating pressure range of 10 to 120 bars was also reported by researchers (Daudin et al., 2010, McCall and Brandvold 2009). The presence of high operating pressure ensures higher solubility of hydrogen in the bio-oil and thereby increases the availability of hydrogen in the vicinity of the catalyst; this also increases the

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reaction rate and further decreases the reactor coking (Venderbosch et al. 2010, Kwon et al. 2011).

Elliot et al. (2009) used an excess of hydrogen of 35 to 420 mol per Kg bio-oil, compared to the requirement of 25 mol/kg for complete deoxygenation (Venderbosch et al. 2010). In a continuous flow reactor, the oxygen content decresed from 21 wt% to 10 wt% when decreasing the LHSV from 0.7 to 0.25 h^{-1} over Pd/C at 340 °C and 140 bar pressure (Elliot 2009). In general LHSV should be in the order of 0.1 to 1.5 h^{-1}. (McCall and Brandvold 2009).

HDO reactivity of bio-oils varies due to the composition of the feedstock and process parameters. Therefore further study is required with bio-oil feed in order to optimize the process parameters. The objective of the research performed in this chapter was to determine the best process conditions (temperature, pressure, hydrogen flow rate (HFR) and liquid hourly space velocity (LHSV)) for application of sulfided CoMo/γ-Al_2O_3 catalyst to hydroprocess raw bio-oil.

3.3 Experimental

3.3.1 Materials

CoMo/γ-Al_2O_3 (3.4-4.5% Co and 11.5-14.5% Mo on gamma-alumina support) was purchased from Alfa Aesar. Cyclohexane and carbondisulfide were purchased from Fisher Scientific. The oxide forms of catalysts was activated by subjecting them to a sulfidation process prior to hydroprocessing experiments. CoMo/γ-Al_2O_3 was sulfided with a solvent mixture of 2 vol % carbon disulfide and cyclohexane. To 800 ml of cyclohexane solvent, 16 ml (2 vol %) of carbon disulfide was added and the solvent mixture was pumped through a high-pressure dual-pump system. Sulfiding of the catalyst

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was performed at 300 °C, a pressure of 750 psi and LHSV of 1 h^{-1} for a period of 4 hrs. Bio-oil was produced by the fast pyrolysis process at a temperature of 400-450 °C under nitrogen gas atmosphere using a 7 kg/h auger-fed pyrolysis reactor located in the Department of Sustainable Bioproducts, Mississippi State University.

3.3.2 Methods

3.3.3 Continuous packed-bed reactor

The continuous packed-bed reactor (Figure 3.1) used in the experimentsconsisted of a 1” I.D tubular reactor enclosed in a three-zone furnace (three 6” zones each independently controlled by its own temperature controller) followed by a condensation system. The temperatures inside the reactor were monitored with a point profile thermocouple equipped with ten sensing points (Omega Instruments). Three temperature sensing points were located in each of the 3 reactor heater zones for a total of 9. The tenth temperature sensing point was located at the condenser orifice. The catalyst bed temperature zones were maintained as closely as possible to the desired temperature set point through the course of the experiment. The catalytic reaction is exothermic such that temperatures are difficult to control due to the adiabatic nature of the reaction. Temperature control was only possible within a temperature range (for example 375-400 °C). The bio-oil was pumped into the catalyst tube with a high pressure dual-pump system (Teledyne Isco 500D). The hydrogen flow rate was controlled with a mass flow controller (MFC; Brooks Instruments), and the reactor pressure was controlled with a back-pressure regulator. A schematic diagram of the reactor is shown in Figure 3.1.

For all experiments the reactor was loaded with catalyst at a temperature initially set to 150 °C. Figure 3.1 shows a diagram of the schematic of the continuous packed- bed

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reactor. Figure 3.2a and 3.2b shows the method of catalyst loading in the continuous packed-bed reactor. For all the experiments reactor was loaded with catalyst at a temperature initially set to 150 °C. Once this initial temperature set point was attained, the reactor temperature was raised by another 100 °C upon reading the resultant temperature of 250 °C and the reactor temperature was again raised to 350 °C. A final 25 to 50 °C increase was often applied to raise the actual reaction temperature as close to 375 °C as possible (for example 375-400 °C). The reactor was pressurized to the desired 1500 psi hydrogen reaction pressure. Hydroprocessing of raw bio-oil was performed in a continuous packed-bed reactor utilizing sulfided CoMo/γ-Al_2O_3 catalyst. Process conditions were varied to determine the most effective temperature (325-350, 375-400, 400-425°C), pressure (1000, 1500 psig), hydrogen flow rate (500, 1000ml/min) and liquid hourly space velocity (0.1, 0.3, 0.7, 1 h^{-1}).

The exit gas flow rate in milliliters per minute (ml/min) was monitored by an Agilent gas flow meter. Products exiting from the packed-bed reactor were cooled in the condenser and the liquid products were collected in a sampling bottle at 2 h intervals. Periodic gas sampling was also performed every 2 h using Tedlar sampling bags. The collected liquid products were centrifuged for 1 h to separate the aqueous fraction (AF) and organic fraction or hydrocarbon fraction (OF or HCF). The experiments were performed over a period of 8 h. Table 3.1 describes the numbered components of the continuous packed-bed reactor provided in Figure 3.1, Figure 3.2a and Figure 3.2b.

Figure 3.2. shows the method of catalyst loading in the continuous packed-bed reactor (a. Method of catalyst loading inside the reactor, enclosed in a furnace b. Inside reactor with loaded catalyst).

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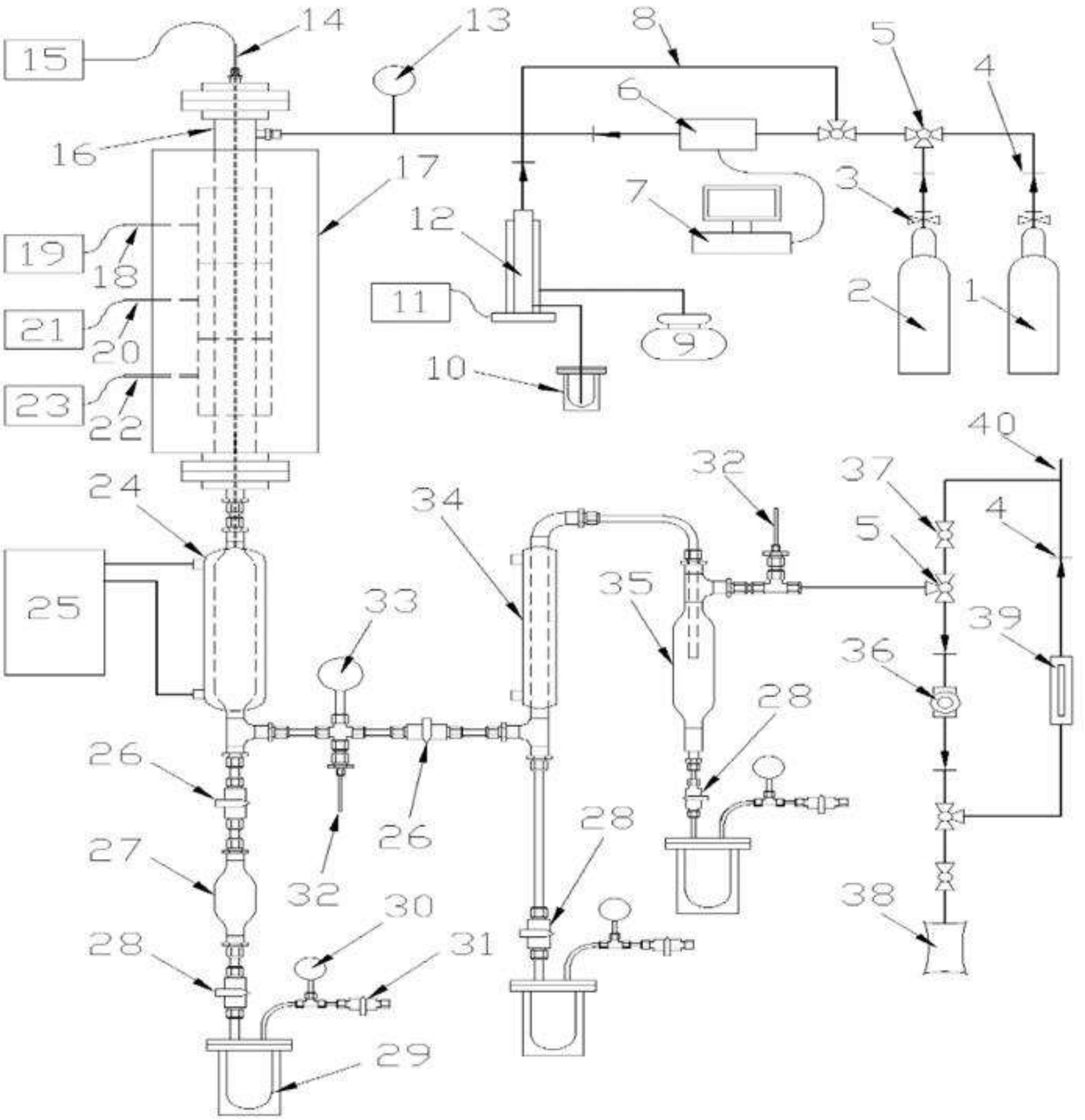

Figure 3.1 Schematic of the continuous packed-bed reactor.

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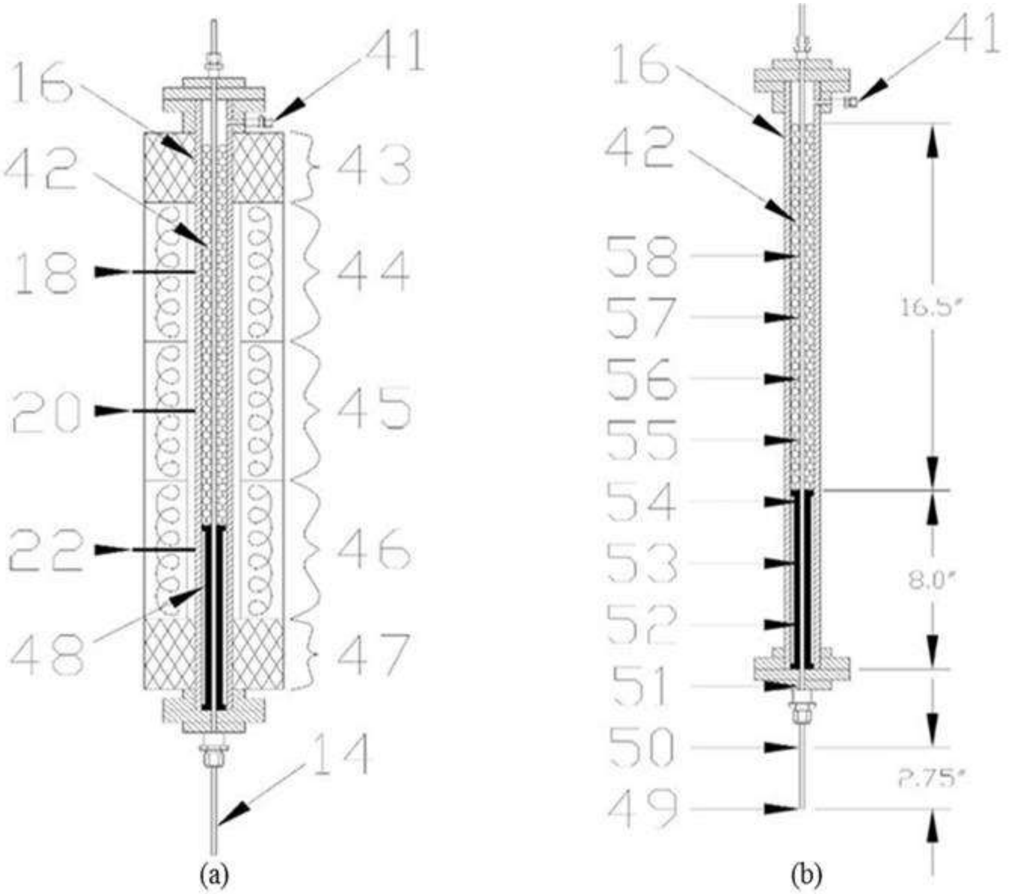

Figure 3.2 Method of catalyst loading in continuous packed-bed reactor

(a. Method of catalyst loading inside the reactor, enclosed in a furnace; b. Inside reactor with loaded catalyst).

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Table 3.1 The numbered components of the continuous packed-bed reactor provided in Figure 5.1 and Figure 5.2 (5.2a and b).

1	Hydrogen cylinder	30	Sampling vessel pressure gauge
2	Air cylinder	31	Sampling vessel ball valve
3	Cylinder regulator	32	Thermocouple
4	Check valve	33	Reactor exit pressure gauge
5	Three-way valve	34	Condenser 2
6	Mass flow controller (MFC)	35	Condenser 3
7	Computer-MFC program	36	Back pressure regulator
8	MFC bypass line	37	Needle valve
9	Air compressor	38	Gas sample bag
10	Bio-oil	39	Exit gas flow meter
11	High pressure pump controller	40	Gas exit line
12	High pressure pump	41	Bio-oil inlet
13	Reactor inlet pressure gauge	42	Catalyst
14	Ten zone reactor thermocouple	43	Heater top insulation, 3" long
15	Ten zone thermocouple monitor	44	Heater zone 1, 6" long
16	Reactor tube	45	Heater zone 2, 6" long
17	Reactor tube heater	46	Heater zone 3, 6" long
18	Heater zone 1 thermocouple	47	Heater bottom insulation, 3" long
19	Heater zone 1 controller	48	Catalyst support
20	Heater zone 2 thermocouple	49	Reactor thermocouple zone 1
21	Heater zone 2 controller	50	Reactor thermocouple zone 2
22	Heater zone 3 thermocouple	51	Reactor thermocouple zone 3
23	Heater zone 3 controller	52	Reactor thermocouple zone 4
24	Condenser 1	53	Reactor thermocouple zone 5
25	Chiller	54	Reactor thermocouple zone 6
26	Ball valve	55	Reactor thermocouple zone 7
27	Hydrocarbons storage vessel	56	Reactor thermocouple zone 8
28	Needle valve	57	Reactor thermocouple zone 9
29	Sampling vessel	58	Reactor thermocouple zone 10

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3.3.4 Physical and chemical analysis

Raw bio-oil (RBO) and the OF produced from the hydroprocessing treatments were characterized following ASTM methods. For the AV test, 1 g of sample was dissolved in isopropanol/water (v/v =35:65) solution and then titrated with 0.1 N NaOH to a pH of 8.5. The AV was then calculated as the required milligrams (mg) amounts of NaOH equivalent to 1 g of sample, according to ASTM D664. The HHV was determined with a Parr 6400 automatic isoperibol calorimeter according to ASTM D240. The Karl Fischer method was employed to determine water content by ASTM E203 with a Cole-Parmer Model C-25800-10 titration apparatus. Elemental analysis (CHNO) for determination of percent carbon (C) percent hydrogen (H), percent nitrogen (N) and percent oxygen (O) were determined by EAI CE-440 elemental analyzer, with oxygen content determined by difference by the ASTM D5291 method. Based on the significantly superior product properties and yields, the OF of best process condition will be chosen for more detailed analysis by detailed hydrocarbon analysis (DHA). DHA was performed by a PerkinElmer Clarus 680 GC equipped with a built-in model Arnel 4060 DHA analyzer, performed by ASTM D6730-01 method, gas chromatography mass spectroscopy (GC-MS) and Fourier transform infrared spectroscopy (FTIR).

3.3.5 Experimental design

Each experiment was performed following 3 replicates. A factorial arrangement of treatments in a completely randomized design was employed with the one factorial being time interval or run time. The analysis of the OF properties produced following process variables/conditions (temperature, pressure, HFR and LHSV), were performed by application of Eq's. 3.1, 3.2, 3.3 and 3.4 with SAS software version 9.3. The analysis of

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variance (ANOVA) model as shown in Eq's. 3.1, 3.2, 3.3 and 3.4, was comprised of one factorial representing run time following with process conditions (temperature, pressure, HFR and LHSV) to determine their influence on physical properties of AV, HHV, oxygen content and WC produced by hydroprocessing of raw bio-oil (RBO). ANOVA Eq's. 3.1, 3.2, 3.3 and 3.4 were also applied to yield analysis. The ANOVA treatment significance satisfied the requirement of Fisher's protected LSD (Steel et al. 1980). The least significant difference (LSD) test was performed to separate the physical property means, run times and yields (Total yields (TY), organic fraction (OF) and aqueous fraction (AF)) as influenced by the run time interval treatments. All statistical tests were performed at the 0.05 level of significance.

The ANOVA model was performed for each of the physical properties, run time and liquid yields.

$$Y_i = \beta_0 + \beta_1 A_i + e_i \qquad \text{Eq. 3.1}$$

Where:

Y_i represents dependent variable physical or chemical testing values: acid value, HHV, oxygen percent, WC, run time and yields,

β_0 represents the intercept term,

$\beta_1 A_i$ represents the influence of temperature (325-350, 375-400 and 400-425 °C) for raw bio-oil by maintaining other variables constant (Pressure 1500 psi, HFR 1000 ml/min and LHSV of 0.3 h^{-1})

e_i represents random error term.

The ANOVA model was performed for each of the physical properties, run time and liquid yields.

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$$Y_i = \beta_0 + \beta_1 A_i + e_i \qquad \text{Eq. 3.2}$$

Where:

Y_i represents dependent variable physical or chemical testing values: acid value, HHV, oxygen percent, WC, run time and yields,

β_0 represents the intercept term,

$\beta_1 A_i$ represents the influence of pressure(1000 and 1500 psi) for raw bio-oil by maintaining other variables constant (temperature 375-400 °C, hydrogen flow rate 1000 ml/min and LHSV of 0.3 h^{-1})

e_i represents random error term.

The ANOVA model was performed for each of the physical properties, run time and liquid yields.

$$Y_i = \beta_0 + \beta_1 A_i + e_i \qquad \text{Eq. 3.3}$$

Where:

Y_i represents dependent variable physical or chemical testing values: acid value, HHV, oxygen percent, WC, run time and yields,

β_0 represents the intercept term,

$\beta_1 A_i$ represents the influence of HFR (500 and 1000 ml/min) for raw bio-oil by maintaining other variables constant (temperature 375-400 °C ,pressure 1500 psi, and LHSV of 0.3 h^{-1})

e_i represents random error term.

The ANOVA model was performed for each of the physical properties, run time and liquid yields.

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$$Y_i = \beta_0 + \beta_1 A_i + e_i \qquad \text{Eq. 3.4}$$

Where:

Y_i represents dependent variable physical or chemical testing values: acid value, HHV, oxygen percent, WC, run time and yields,

β_0 represents the intercept term,

$\beta_1 A_i$ represents the influence of LHSV (0.1, 0.3, 0.7 and 1.0 h^{-1}) for raw bio-oil by maintaining other variables constant (temperature 375-400 ºC, pressure 1500 psi and hydrogen flow rate 1000)

e_i represents random error term.

The effect of process conditions were compared by the LSD comparison of means method performed for physical properties (AV, HHV, oxygen content and WC); runtimes and yields (TY, AF and OF or HCF) were also independently tested by LSD method. The 3 replicate values for the best treatment were included in the test to determine the influence of process conditions in terms of OF properties and yields. Fisher's protected LSD test for ANOVA significance multiple comparison of means were performed by LSD for each physical property (AV, HHV, WC, oxygen content). Properties and yields were also tested in an ANOVA with Fisher's protected LSD test performed to determine significance.

3.4 Results and Discussion

3.4.1 Testing of different process conditions

Sulfided CoMo/γ-Al_2O_3 catalyst was tested as the hydroprocessing catalyst at various process conditions: temperature (T), pressure (P), hydrogen flow rate (HFR) and liquid hourly space velocity (LHSV). Three temperature ranges, 325-350 °C, 375-400 °C,

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400-425 °C, and two pressures of 1000 and 1500 psig, two HFRs of 500 ml/min and 1 ltr/min and LHSV's of 0.1, 0.3, 0.7 and 1 h^{-1} were tested in several combinations for a total of 11 treatments as shown in Table 3.2. The combinations were arrived at by testing all three temperatures at a P of 1500 psig, an HFR of 1000 ml/min and LHSV of 0.3 h-1. Of the three different temperature treatments tested the temperature that provided the best HCF yield and its properties was selected as that applied for testing the pressure, HFR and LHSV conditions. All remaining treatments were also compared and the best performing treatment was also selected by choosing the treatment with the best HCF yield and it properties. For the best-performing temperature the hydrogen pressure variable was tested at 1000 psig and 1500 psig which provided two more treatments. For the best performing pressure two HFR treatments (500 and 1000 ml/min) were tested giving another two treatments. The HFR with the best performance was selected and treated with four levels of LHSV. Liquid and gas samples were collected at intervals and were subjected to analysis. RBO was the feedstock for the hydroprocessing (hydrotreating and hydrocracking performed in a single step) process. The hydroprocessing reaction was performed in a continuous packed bed reactor.

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Table 3.2 The temperature, pressure, hydrogen flow rate (HFR) and liquid hourly space velocity (LHSV) treatment combinations applied.

Treatment number (T.No)	Temperature (°C)	Pressure (psig)	HFR (ml/min)	LHSV ($h-^1$)
0 (RBO)	NA	NA	NA	NA
1	325-350	1500	1000	0.3
2	375-400	1500	1000	0.3
3	400-425	1500	1000	0.3
4	375-400	1000	1000	0.3
5	375-400	1500	1000	0.3
6	375-400	1500	500	0.3
7	375-400	1500	1000	0.3
8	375-400	1500	1000	0.1
9	375-400	1500	1000	0.3
10	375-400	1500	1000	0.7
11	375-400	1500	1000	1

Tables 3.3, 3.4 and 3.5 and Figure 3.3 describe the properties of OF obtained by the hydroprocessing of the RBO by the hydroprocessing teatments to determine the effect of temperature (325-350, 375-400 and 425-450 °C) by maintaining other variables, pressure (1500 psi), HFR (1000 ml/min) and LHSV (0.3 h^{-1}) constant. The properties of RBO (treatment 0) are given in Table's 3.3, 3.4 as the control to allow comparison of the RBO properties to the upgraded properties from the treatments. The AV values of the treated bio-oils are only a small fraction, 4.1 and 0.7%, of the AV value (96.4 mg of KOH/g) of the RBO. The lowest AV of the three variable temperature treatments was 0.67 (0.7% of the RBO AV) for the temperature treatment of 375-400 °C, pressure of 1500 psig, HFR of 1000 ml/min and LHSV of 0.3. The highest HHV was 44.0 MJ/kg for

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the temperature treatment of 375-400 ^{o}C. The properties of the OF were also compared to determine if the highest yielding treatment had satisfactory properties.

The CHNO properties produced differed little with one exception for the O value of treatment 1 (temperature of 325-350 ^{o}C). The O value of this treatment was 4.0% which is a very high value compared to the values for treatments 2 and 3 (0.09 and 0.0%) for the respective temperature values of 375-400 and 400 to 425 ^{o}C. Results of OF (AV, HHV, CHNO, %WC, TL, HCF and AF) at three temperatures (325-350, 375-400, 400-425 ^{o}C).

Table 3.3 Results of OF (AV, HHV, CHNO, %WC, TL, HCF and AF) at three temperature's (325-350, 375-400, 400-425 ^{o}C).

T.No	Temp (^{o}C)	AV (mg of KOH/g)	HHV (MJ/Kg)	C %	H %	N %	O %	WC %
0	RBO	96.5 (a)	16.5 (d)	37.3 (d)	7.7 (d)	0.6 (a)	54.5 (a)	28.9 (a)
1	325-350	4.1 (b)	41.6 (c)	83.7 (c)	12.0 (c)	0.3 (c)	4.0 (b)	0.5 (b)
2	375-400	0.7 (c)	44.0 (a)	87.1 (a)	13.0 (a)	0.3 (c)	0.1(c)	0.1 (c)
3	400-425	4.1 (b)	42.9 (b)	86.9 (b)	12.8 (b)	0.4 (b)	0 (d)	0.1 (c)

(of sulfided CoMo/γ-Al_2O_3 catalysis of raw bio-oil for three temperatures's, pressure of 1500 psig, LHSV of 0.3 h-1 and HFR of 1000 ml/min).

The percentage WC properties for treatments 2 and 3 (375-400 and 400 to 425 ^{o}C) were both 0.1%. However, the percentage value for treatment 1 (325-350 ^{o}C) was 5 times higher at 0.5%. The OF yield was higher for treatment 2, which was 24.6% compared to 20.3% and 24.4% HCF yield for the respective treatments 2 (375-400 ^{o}C) and 3 (400-425 ^{o}C). From Tables 3.3, 3.4 and 3.5 and Figure 3.3, based on properties and HCF yield, treatment 2 (375-400 ^{o}C) was considered as the best temperature treatment. And the gas

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consumption was almost the same at below tested temperatures. This temperature was chosen for further treatment variable type (pressure, HFR and LHSV) studies.

Table 3.4 Yields of OF at three temprature's (325-350, 375-400, 400-425 ºC).

T.No	Yields wt%	TL wt%	OF wt%	AF wt%
1	325-350	75.1 (c)	20.3 (c)	54.9 (b)
2	375-400	85.2 (a)	24.6 (a)	60.5 (a)
3	400-425	77.4 (b)	24.4 (b)	53.0 (c)

(at pressure of 1500 psig, LHSV of 0.3 h-1 and HFR of 1000 ml/min).

Table 3.5 Gas analysis of three temperature's (325-350, 375-400, 400-425 ºC).

T.No	Temp (ºC)	H_2 %	O_2 %	N_2%	CH_4 %	CO %	CO_2 %	C_2H_6 %
1	325-350	75.1	0.8	2.5	0.3	0	0.3	0.3
2	375-400	76.1	0.4	1.3	0.1	0.1	1.6	1
3	400-425	73.2	0.5	1.5	2	0.1	1.5	1.3

(at pressure of 1500 psig, LHSV of 0.3 h-1 and HFR of 1000 ml/min).

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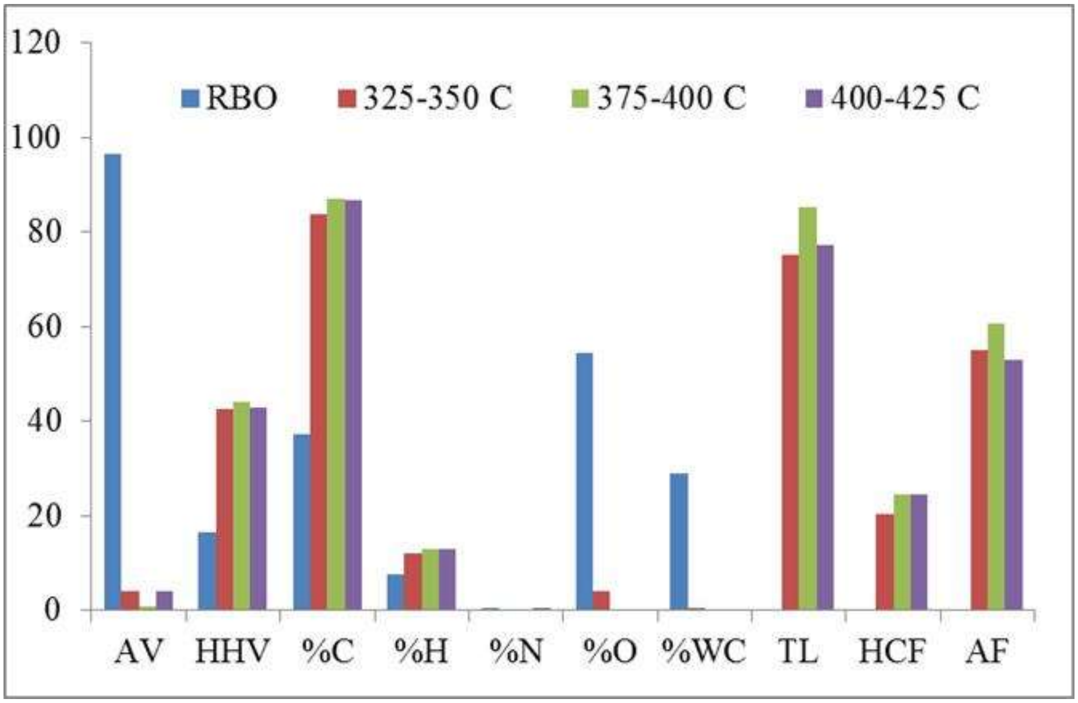

Figure 3.3 Results (AV, HHV, CHNO, %WC, TL, HCF and AF) at three temperatures (of sulfided CoMo/γ-Al_2O_3 catalysis of raw bio-oil for three temperatures's, pressure of 1500 psig, LHSV of 0.3 h^{-1} and HFR of 1000 ml/min).

Tables 3.6, 3.7 and 3.8 and Figure 3.4 describes the properties of HCF obtained by hydroprocessing treatments of RBO to determine the effect of pressure (1000 and 1500 psi) by maintaining other variables, temperature (375-400 ºC), HFR (1000 ml/min) and LHSV (0.3 h^{-1}) constant. Again, as for the pressure value of treatments 5 (1500 psi), the AV values of the treated RBO's are only a small fraction, 2.9 and 0.7%, of the AV value (96.4 mg of KOH/g) of the RBO. The lowest AV and highest HHV were for treatment 5 at 0.67 mg KOH/g (0.7% of the RBO AV) and 44.0 MJ/kg (44.0% of the RBO HHV) for the treatment 5 (temperature of 375-400 ºC, P of 1500 psig, HFR of 1000 ml/min and LHSV of 0.3 h^{-1}). No difference in % WC (0.1 and 0.1%) was observed for both treatments 4 and 5. Treatment 5 was chosen as having the best performance

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based on the HCF yield of 24.6% compared to 20.8% HCF yield (Table 3.7). The gas consumption was high incase of treatment 4 (1000 psig pressure). From the tested pressure treatment variables 4 and 5 (1000 and 1500 psig pressure) based on HCF yields and properties, treatment 5 (1500 psig) was considered as the best treatment for pressure. This pressure was chosen for further treatment variable type (HFR and LHSV) studies.

Table 3.6 Results of OF (AV, HHV, CHNO, %WC, TL, HCF and AF) at two pressures (1000 and 1500 psi).

T.No	Pressure (psig)	AV (mg of KOH/g)	HHV (MJ/Kg)	C %	H %	N %	O %	WC %
0	RBO	96.5 (a)	16.5 (c)	37.3 (a)	7.7 (c)	0.6 (a)	54.5 (a)	28.9 (a)
4	1000	2.9 (b)	41.6 (b)	86.6 (b)	12.7 (b)	0.4 (b)	0.3 (b)	0.1 (b)
5	1500	0.7 (c)	44.0 (a)	87.1 (a)	13.0 (a)	0.3 (c)	0.1 (c)	0.1 (b)

(for a temperature of 375-400 °C two pressures, LHSV of 0.3 h-1 and HFR of 1000 ml/min in presence of sulfided CoMo/γ-Al_2O_3 catalyst).

Table 3.7 Yields of OF for two pressures (1000 and 1500 psi).

T.No	Pressure (psig)	TL wt%	HCF wt%	AF wt%
4	1000	73.8 (a)	20.8 (b)	53.0 (b)
5	1500	85.2 (a)	24.6 (a)	60.5 (a)

(at temperature of 375-400 °C, LHSV of 0.3 h^{-1} and HFR of 1000 ml/min).

Table 3.8 Gas analysis for a T of 375-400 °C, two pressures, LHSV of 0.3 h^{-1} and HFR of 1000 ml/min.

T.No	Pressure (Psig)	H_2 %	O_2 %	N_2%	CH_4 %	CO %	CO_2 %	C_2H_6 %
4	1000	53.9	0.6	8.2	2.2	0.2	3.9	1.8
5	1500	76.1	0.4	1.3	0.1	0.1	1.6	1.0

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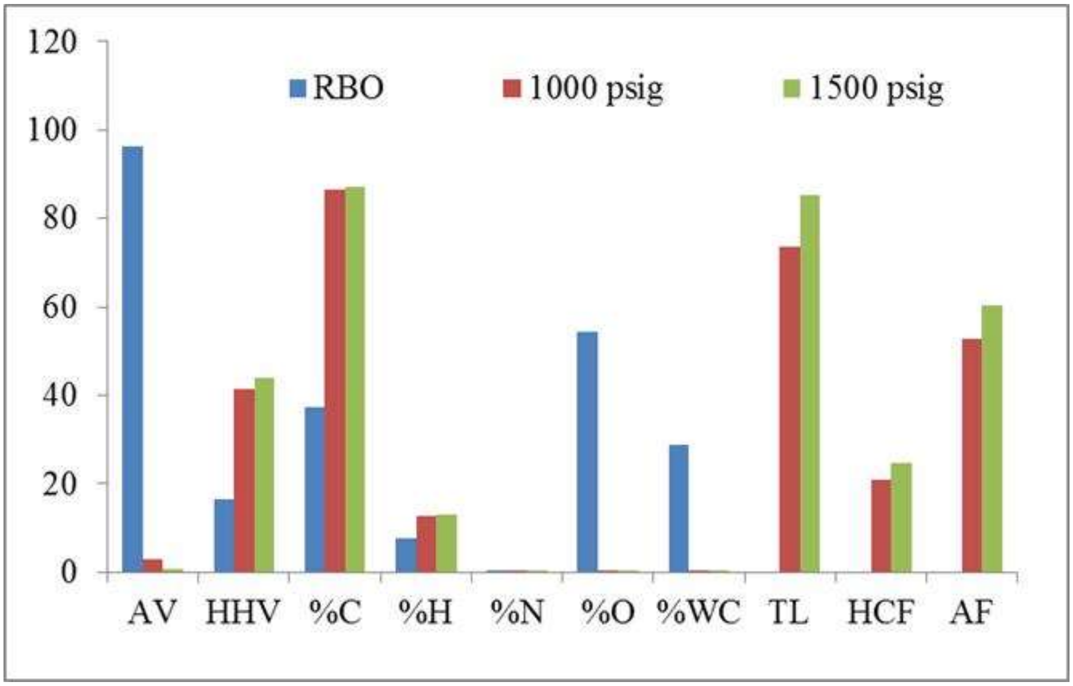

Figure 3.4 Results (AV, HHV, CHNO, %WC, TL, HCF and AF) at two pressures (1000, 1500 psi).

(at temperture of 375-400 °C, LHSV of 0.3 h^{-1} and HFR of 1000 ml/min).

Tables 3.9, 3.10 and 3.11 and Figure 3.5 describes the properties of HCF obtained by the hydroprocessing of the RBO by the hydroprocessing treatments to determine the effect of HFR (500 and 1000 ml/min), by maintaining other variables, temperature (375-400 °C), pressure (1500 psi) and LHSV (0.3 h^{-1}), constant. These experiments were performed utilizing the previously tested best temperature (375-400 °C) and pressure (1500 psi). The respective AV values of treatments 6 and 7 (375-400 °C, P of 1500 psig, HFR of 1000 ml/min and LHSV of 0.3) were much lower at 4.3 mg and 0.67 mg/g KOH than the RBO AV value (96.4 mg of KOH/g). The treatment 6 AV value at 4.3 mg KOH/g was more than 6 times higher than the treatment 7 value of 0.67 mg KOH/g. The HHV for treatment 6 was 43.0 MJ/kg with treatment 7 slightly higher at 44.0 MJ/kg. The CHNO properties differed little between treatments 6 and 7 (500 and 1000 ml/min HFR).

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The O value of treatment 6 was 1.8% which was 18 times higher than the 0.1% value for treatment 7. The percentage WC values were 2.1 and 0.1% for treatments 6 and 7, respectively. The HCF yield was somewhat higher for treatment 6 (26.1%) compared to treatment 7 (24.6%). Therefore the major differences between treatments 6 and 7 were 6 times as much AV for treatment 6, 18 times as much oxygen. The only superior property of treatment 6 was that it yielded slightly higher (1.5 wt%) HCF than for treatment 7. The best treatment based on most of the property comparisons was treatment 7. Therefore, the HFR of 1000 ml/min for treatment 7 was selected as the best HFR compared to the 500 ml/min for treatment 6.

Table 3.9 Results of OF (AV, HHV, CHNO, %WC, TL, HCF and AF) for two HFR's (500, 1000 ml/min).

T.No	HFR (ml/min)	AV (mg of KOH/g)	HHV (MJ/Kg)	C %	H %	N %	O %	WC %
0	RBO	96.5 (a)	16.5 (c)	37.3 (c)	7.7 (c)	0.6 (a)	54.5 (a)	28.9 (a)
6	500	4.3 (b)	43.0 (b)	85.3 (b)	12.5 (b)	0.6 (a)	1.8 (b)	2.1 (b)
7	1000	0.7 (c)	44.0 (a)	87.1 (a)	13.0 (a)	0.3 (b)	0.1 (c)	0.1(c)

(at temperature of 375-400 °C, pressure of 1500 psig and LHSV of 0.3 h^{-1}).

Table 3.10 Yields for two HFR's, temperature of 375-400 °C, pressure of 1500 psig and LHSV of 0.3 h^{-1}.

T.No	HFR (ml/min)	TL wt %	OF wt%	AF wt%
6	500	84.9 (b)	26.1 (a)	58.8 (b)
7	1000	85.2 (a)	24.6 (b)	60.5 (a)

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Table 3.11 Gas analysis for two HFR's, temperature of 375-400 °C, pressure of 1500 psig and LHSV of 0.3 h^{-1}.

T.No	HFR (ml/min)	H_2 %	O_2 %	N_2%	CH_4 %	CO %	CO_2 %	C_2H_6 %
6	500	80.7	0.5	1.5	0.3	0	0.24	0.1
7	1000	76.1	0.4	1.3	0.1	0.1	1.6	1

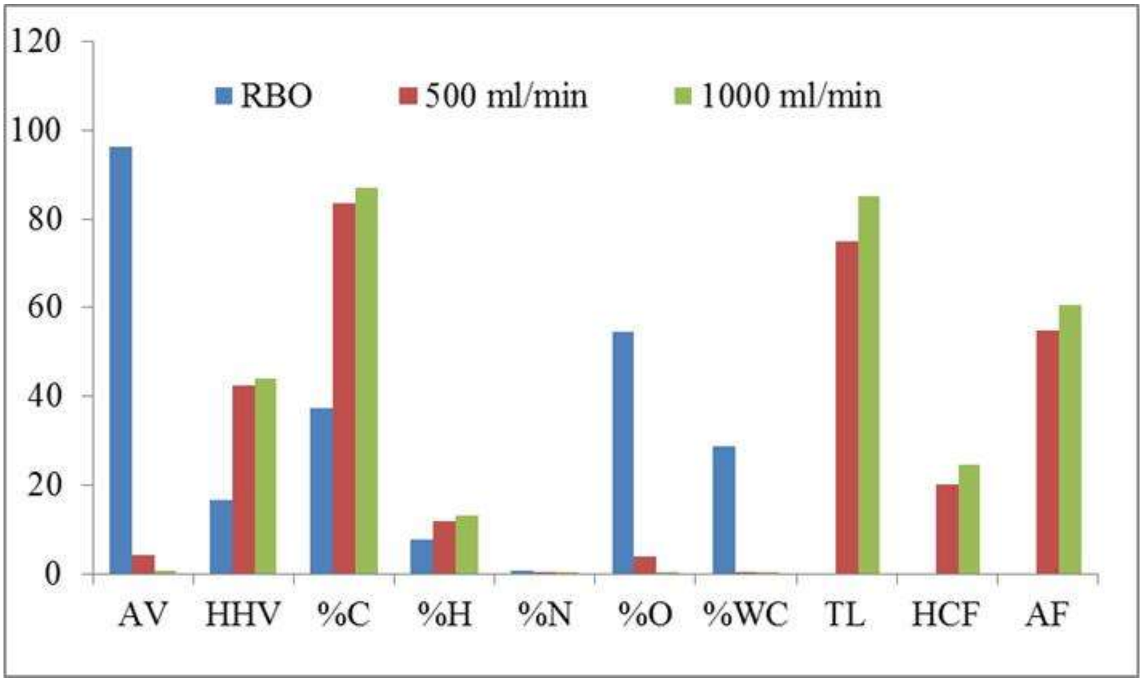

Figure 3.5 Results of OF of (AV, HHV, CHNO, %WC, TL, HCF and AF) for two HFR's.

(at temperature of 375-400 °C, pressure of 1500 psig and LHSV of 0.3 h^{-1}).

Tables 3.12, 3.13 and 3.14 and Figure 3.6 describes the properties of HCF obtained by the hydroprocessing of the RBO by the hydroprocessing treatments to determine the effect of LHSV (0.1, 0.3, 0.7 and 1.0 h^{-1}) by maintaining other variables, temperature (375-400 °C), pressure (1500 psi) and HFR (1000 ml/min) constant. As described above the HFR for treatment 7 (1000 ml/min) was selected as the best

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performing treatment. Treatments 8 and 9 utilized this HFR and previously selected best temperature and pressure (375-400 ºC, P of 1500 psig). Treatments 8, 9, 10 and 11 varied the LHSV to 0.1 and 0.3 h^{-1} to determine the relative effects. The results of treatments 8 and 9 are shown in Tables 3.12, 3.13 and 3.14 and Figure 3.6. The AV values of treatments 8, 9, 10 and 11 applied to RBO were again greatly reduced compared to the 96.4 mg KOH/g at 0.7, 0.7, 17.8 and 32.1%. The percentage of the respective HCF yields for treatments 8 and 9 were 14.1 and 24.6%.The highest HHV was 43.7 and 44.0 MJ/kg for the varied LHSV treatments 8 and 9 (0.1 and 0.3 h^{-1}), respectively. The properties of HCF obtained from both treatments 8 and 9 differed little in terms of CHNO and water content percentage. Therefore, the selection of the best treatment from treatments 8, 9, 10 and 11 could be made based on its much higher yield (77.4% higher for treatment 9 at 24.6%). The treatments did not differ much in gas consumption, with the exception of treatment 11. Whereas, with increase in LHSV to 0.7 and 1.0 h^{-1} though yielded high HCF (27.6 and 32.3% respectively), the product quality is not satisfactory in terms of properties (AV (17.8 and 32.1 mg KOH/g, respectively), HHV (38.7 and 35.4 MJ/kg, respectively), oxygen content (13.0 and 16.8% respectively) and WC percentage (3.7 and 4.4%).

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Table 3.12 Results of OF (AV, HHV, CHNO, %WC, TL, HCF and AF) for four LHSV's (0.1, 0.3, 0.7, 1.0 h^{-1}).

T.No	LHSV (h^{-1})	AV (mg of KOH/g)	HHV (MJ/Kg)	C %	H %	N %	O %	WC %
0	RBO	96.5 (a)	16.5 (e)	37.3 (e)	7.7 €	0.6 (a)	54.5 (a)	28.9 (a)
8	0.1	0.7 (d)	43.7 (b)	85.4 (b)	14.3 (a)	0.4 (b)	0 (e)	0.1 (d)
9	0.3	0.7 (d)	44.0 (a)	87.1 (a)	13.0 (b)	0.3 (c)	0.1 (d)	0.1 (d)
10	0.7	17.8 (c)	38.7 (c)	78.7 (c)	10.3 (c)	0.3 (c)	13.0 (c)	3.7 (c)
11	1	32.1 (b)	35.4 (d)	78.1 (d)	10.0 (d)	0.2 (d)	16.8 (b)	4.4 (b)

(at temperature of 375-400 °C, pressure of 1500 psig and HFR of 1000 ml/min.

Table 3.13 Yields for four LHSV's, temperature of 375-400 °C, pressure of 1500 psig and HFR of 1000 ml/min.

T.No	LHSV (h-1)	TL	OF	AF
8	0.1	71.6 (d)	14.1 (d)	57.5 (c)
9	0.3	85.2 (c)	24.6 (c)	60.5 (a)
10	0.7	87.1 (b)	27.6 (b)	59.5 (b)
11	1	87.2 (a)	32.2 (a)	54.9 (d)

Table 3.14 Gas analysis for four LHSV's, temperature of 375-400 °C, pressure of 1500 psig and HFR of 1000 ml/min.

T.No	LHSV (h^{-1})	H_2 %	O_2 %	N_2%	CH_4 %	CO %	CO_2 %	C_2H_6 %
8	0.1	78.8	0.6	2	1.2	0	0.4	0.87
9	0.3	76.1	0.4	1.3	0.1	0.1	1.6	1
10	0.7	76.4	0.9	3.1	0.3	0	0.5	0.3
11	1	70.5	1.0	9.0	0.2	0	0.2	0.2

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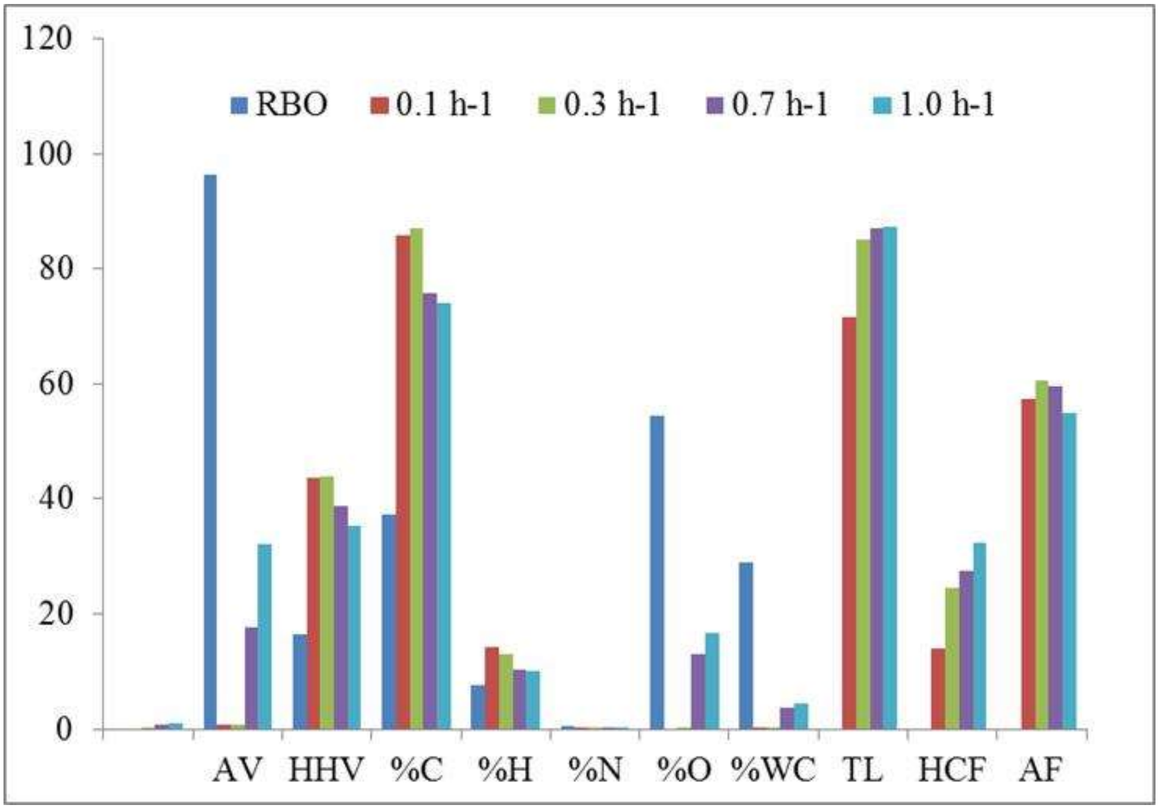

Figure 3.6 Results of OF (AV, HHV, CHNO, %WC, TL, HCF and AF) for four LHSV's (0.1, 0.3, 0.7 and 1.0 h^{-1}).

(at temperature of 375-400 °C, pressure of 1500 psig and HFR of 1000 ml/min).

Table 3.15 Yields (OF, AF and gas), hydrogen consumption and hydrogen conversion for the experiment performed at most effective processs condition.

Yields on dry basis	Units
Oil yield	0.35g/g feed (dry basis)
Aqueous	1.0 g/g feed (dry basis)
Gas	0.1 g/g feed (dry basis)
Char	8 to 10 wt%
Hydrogen consumption	581.5 ml/min
Hydrogen conversion	41.90%

Table 3.15 shows, for the most effective process conditions for the sulfided CoMo/γ-Al_2O_3 catalyst were for a temperature of 375-400 °C, pressure of 1500 psig,

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liquid hourly space velocity of 0.3 h^{-1} and hydrogen flow rate of 1000 ml/min. showed the yields (OF, AF and gas yields) based on dry basis were 0.35, 1.0 and 0.1 g/g feed respectively. The hydrogen consumption and hydrogen conversion for sulfided CoMo/γ-Al_2O_3 was 41.9% and 581.5 ml/min. Higher hydrogen consumption indicates higher deoxygenation.

3.4.2 DHA Analysis

Figure 3.7 shows the DHA of mixed liquid hydrocarbons obtained with sulfided CoMo/γ-Al_2O_3 from the most effective process conditions (temperature of 375-400 °C, pressure of 1500 psig, LHSV of 0.3 h^{-1} and HFR of 1000 ml/min), perfomed according to ASTM D6730-01. The DHA of the upgraded product predominately contained iso-paraffins, naphthenes, compounds greater than C14 and olefins. The other compounds that are identified in minor amounts in comparison to iso-paraffins, olefins, naphthenes and compounds greater than C14 are aromatics and paraffins. The DHA analysis of the hydroprocessed product obtained at the most effective process conditions (temperature of 375-400 °C, pressure of 1500 psig, liquid hourly space velocity of 0.3 h^{-1} and hydrogen flow rate of 1000 ml/min) showed an octane value of 50.3.

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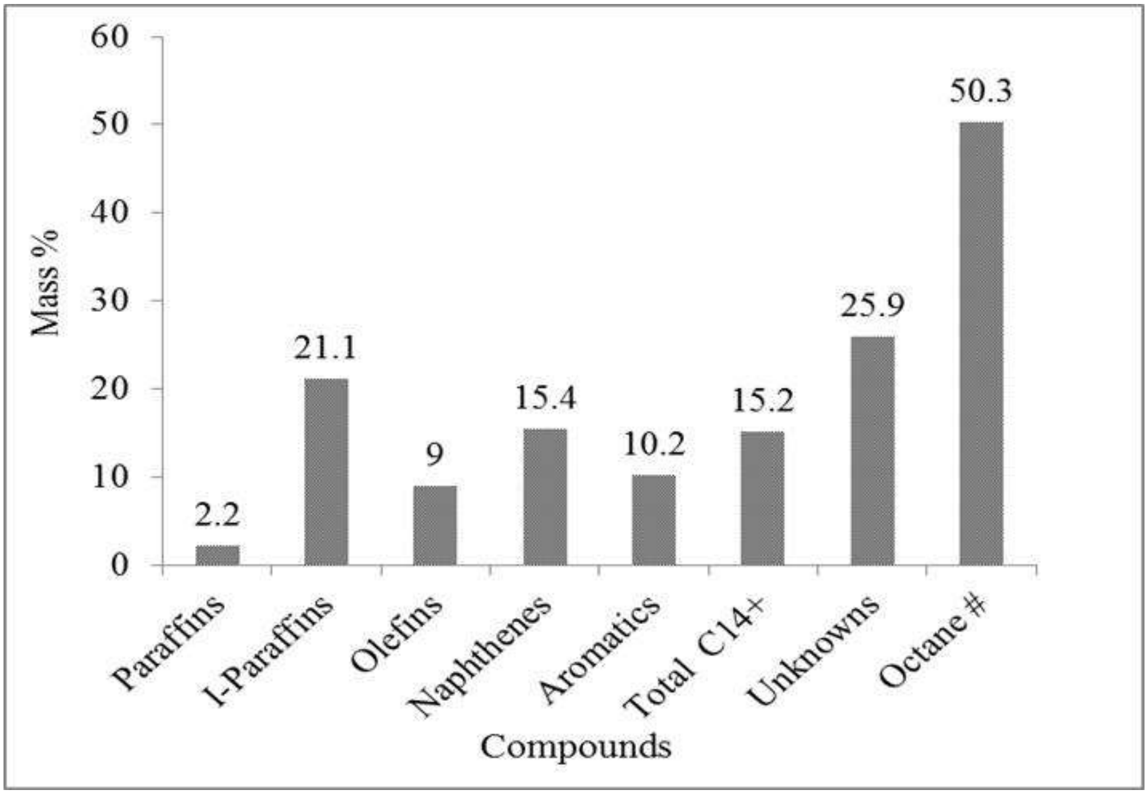

Figure 3.7 DHA of mass percentage (%) of OF obtained hydroprocessed product from sulfided CoMo/γ-Al_2O_3 catalyst from most effective process conditions

(temperature of 375-400 °C, pressure of 1500 psig, LHSV of 0.3 h^{-1} and HFR of 1000 ml/min).

3.4.3 FTIR

FTIR spectral data was used to analyze the raw bio-oil and hydroprocessed product sample obtained at the most effective process conditions (temperature of 375-400 °C, pressure of 1500 psig, LHSV of 0.3 h^{-1} and HFR of 1000 ml/min). Characteristic vibrational modes are observed at 3200-3600 cm^{-1} (OH stretching), 2850-2980 cm^{-1} (CH stretching, aliphatic), 1710 cm^{-1} (C=O stretching), 1375-1475 cm^{-1} (C–H vibrations) and 1100-1300 cm^{-1} (C-O stretching). From Figure 3.8, it was evident that after hydroprocessing, the OH stretching was decreased due to a decrease of oxygenated compounds such as carboxylic acids, water and alcohols present in raw bio-oil. The

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increase of C=O and C-O stretching peaks indicates the presence of oxygenated compounds in the bio-oil. The increase in intensity of 2850-2980 cm^{-1} (CH stretching, aliphatic) 1375-1475 cm^{-1} (C–H vibrations) and CH bending stretch were significantly increased. This change in the absorption band indicates that the carboxylic acids, aldehydes and other oxygenated compounds were converted into hydrocarbons. The FTIR spectral data shown in Figure 3.8 was in good agreement with the physical and chemical properties.

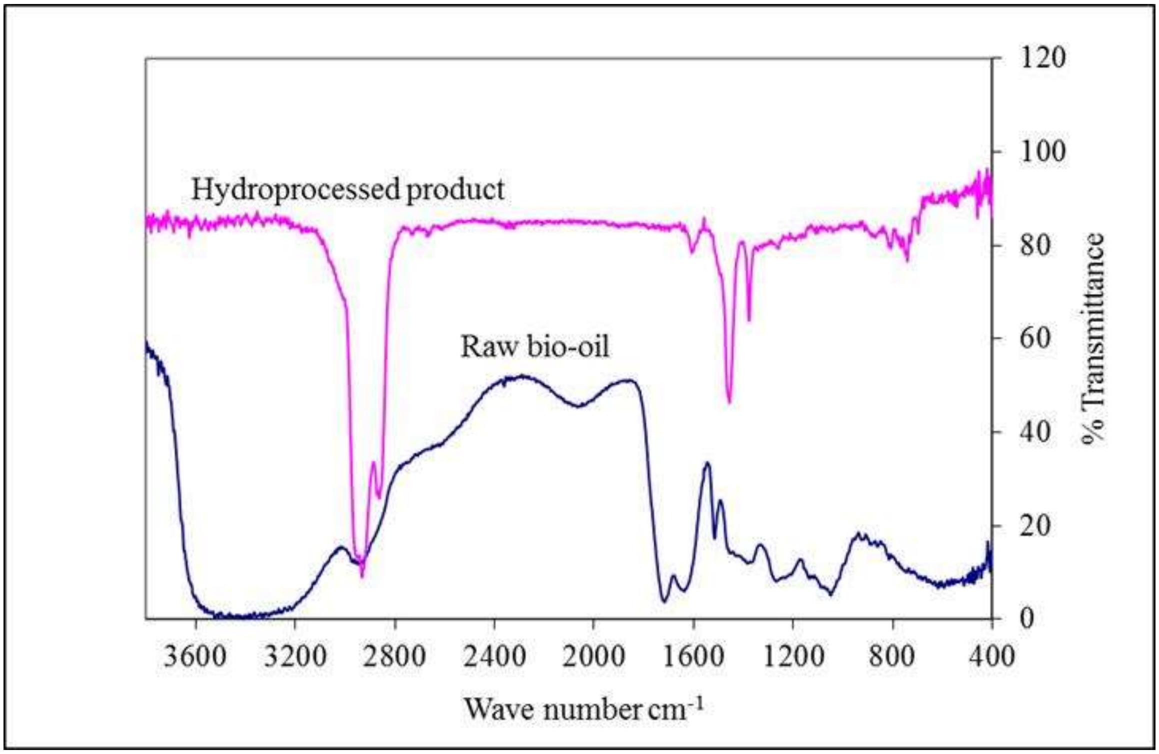

Figure 3.8 FTIR spectral comparison of raw bio-oil and hydroprocessed product obtained from most effective process conditions.

(temperature of 375-400 °C, pressure of 1500 psig, liquid hourly space velocity of 0.3 h^{-1} and hydrogen flow rate of 1000 ml/min).

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3.4.4 Thermogravimetric Analysis (TGA)

TGA was performed on the used catalysts to determine the amount of residual carbon deposited on the catalyst surface. A Shimadzu instrument TGA-50 was used to perform the TG analysis. A required amount of catalyst was placed in an alumina pan and a temperature program was ramped up at a rate of 5 °C/min starting at room temperature and terminating at 800 °C. The runs were performed under air flow of 50 mL/min. The percentage weight loss of the fresh CoMo/γ-Al_2O_3, fresh sulfided CoMo/γ-Al_2O_3 and those of spent CoMo/γ-Al_2O_3 catalyst from the most effective process conditions (temperature of 375-400 °C, pressure of 1500 psig, liquid hourly space velocity of 0.3 h^{-1} and hydrogen flow rate of 1000 ml/min) are shown in Figure 3.9, 3.10 and 3.11.

Figures 3.9, 3.10 and 3.11 show significant loss during the intial heating period at the temperature range between 100 to 220 ºC. This weight loss was due to the removal of moisture from the catalyst surface and also moisture from the interior of the pores. Part of the weight loss could also be due to the removal of easily oxidizable carbonaceous species formed during initial decomposition of the aromatic compounds. Further the water which was bound with the catalyst material requires higher temperature for desorption. In the case of TGA analysis of fresh CoMo/γ-Al_2O_3 (Figure 3.9) and fresh sulfided CoMo/γ-Al_2O_3 (Figure 3.10) no weight loss was observed due to carbon deposition. However, in the case of spent CoMo/γ-Al_2O_3 (Figure 3.11) catalyst from the most effective process conditions (temperature of 375-400 °C, pressure of 1500 psig, liquid hourly space velocity of 0.3 h^{-1} and hydrogen flow rate of 1000 ml/min), weight loss was expected but, in contrast, not much weight loss was observed only 1.2 mg of

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weight loss was observed at a temperature between 375 to 660 °C, which indicates that there was only a slight carbon deposition on the surface of the catalyst.

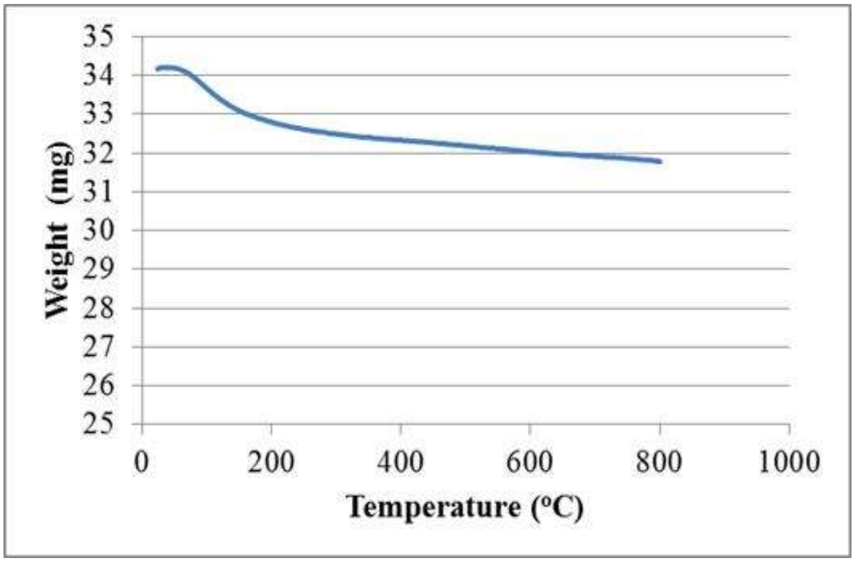

Figure 3.9 TGA of the fresh CoMo/γ-Al_2O_3 catalyst.

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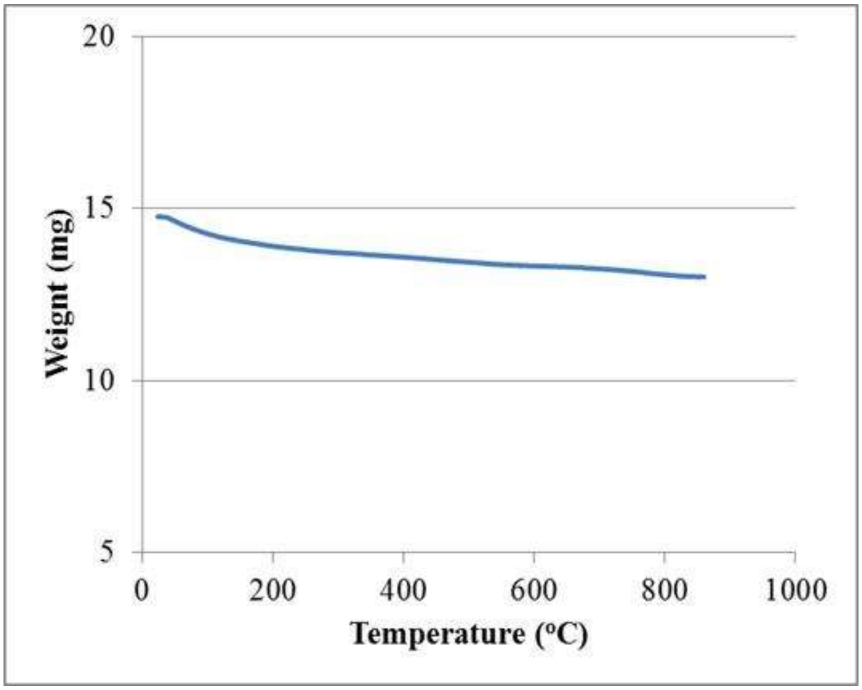

Figure 3.10 TGA of the sulfided CoMo/γ-Al_2O_3 catalyst.

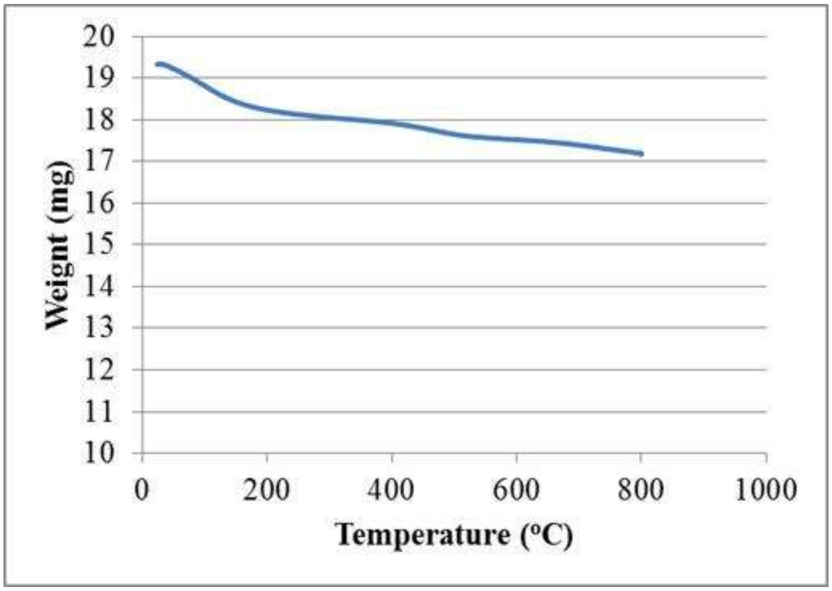

Figure 3.11 TGA of the used CoMo/γ-Al_2O_3 catalyst from most effective process conditions

(temperature of 375-400 °C, pressure of 1500 psig, liquid hourly space velocity of 0.3 h^{-1} and hydrogen flow rate of 1000 ml/min).

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3.5 Conclusion

The results of the described experiments showed that of the tested process variables a temperature of 375-400 °C, pressure of 1500 psig, LHSV of 0.3 h^{-1} and HFR of 1000 ml/min produced both higher yields and satisfactory properties. The product properties of the hydroprocessed RBO for the best combination of treatment conditions were an AV of 0.7 mg of KOH/g, HHV of 44.01 MJ/kg, and percentage WC of 0.1%. The CHNO properties were 87.0, 13.0, 0.3 and 0.1%, respectively. The yields of TL, HCF and AF were 85.1, 24.6 and 60.6 respectively.

The DHA of the upgraded product predominately contained iso-paraffins, naphthenes, compounds greater than C14 and olefins. The other compounds that are identified in minor amounts in comparison to iso-paraffins, olefins, naphthenes and compounds greater than C14 are aromatics and paraffins. The DHA analysis of the hydroprocessed product obtained at the most effective process conditions (temperature of 375-400 °C, pressure of 1500 psig, LHSV of 0.3 h^{-1} and HFR of 1000 ml/min) showed an octane value of 50.3. From TGA analysis not much catalyst weight was observed in the case of spent catalyst. Further catalyst deactivation and regeneration studies will be performed based on, temperature of 375-400 °C, pressure of 1500 psig, LHSV of 0.3 h^{-1}, and HFR of 1000 ml/min (T. No's of 2, 5, 7 and 9) experimental process conditions.

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CHAPTER IV

SINGLE STAGE HYDROPROCESSING OF PYROLYSIS OIL IN A CONTINUOUS PACKED-BED REACTOR

4.1 Abstract

Raw bio-oil cannot be combusted as transportation fuel directly because of its high acidity, high water content, lower heating value and variable viscosity over time. Therefore, bio-oil should be chemically converted to a more stable liquid product before subjecting it to hydrodeoxygenation conditions. This research focused on catalytic hydroprocessing of pretreated bio-oil (PTBO) in a single-stage reaction using various catalyst compositions in a packed-bed reactor. Four catalysts, a conventional hydrotreating CoMo/γ-Al_2O_3, an Fe-Cr based mixed oxide catalyst, an FeW/Si-Al catalyst, and a 1:2 mixture of Ru/γ-Al_2O_3 and Ni/Si-Al catalyst, were tested for conversion of the PTBO to mixed liquid hydrocarbons at 350-400 °C, 1500 psig hydrogen pressure, and at a liquid hourly space velocity of 0.2-0.3 h^{-1}. Liquid products produced from the hydrodeoxygenation treatments were analyzed for properties such as acid value, heating value, elemental analysis, water content, and chemical characterization (GC-MS). The conventional hydrotreating catalyst, CoMo/γ-Al_2O_3, performed the best among the four catalysts employed in significantly reducing the acid value to 2 mg KOH/g and oxygen content to 0.06% while improving the heating value to 43 MJ/Kg of the liquid product. The detailed hydrocarbon analysis of the reduced

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CoMo/γ-Al_2O_3 upgraded hydrocarbon mixture showed the presence of olefins, iso-paraffins, followed by naphthenes and aromatics. Simulated distillation results indicated that the liquid fuel had a boiling point range of 69-304 °C, indicating the presence of petroleum equivalents of 50% gasoline (38 -170 °C), 30% jet fuel (170-250 °C) and 20% diesel (250-304 °C) range hydrocarbons.

4.2 Introduction

Biomass, due to its high carbon value, renewability, and environmentally benign nature, has attracted interest as a potential alternative fuel resource. Fast pyrolysis, a thermo-chemical technology performed at temperatures from 400-550 °C in the absence of oxygen, is an economical route to convert lignocellulosic biomass to a liquid fuel called bio-oil (Carlson et al., 2009, Demiral and Sensoz 2008, Mohan et al., 2006, Elliot 2007). The yields of bio-oil obtained from fast pyrolysis range from 60 to 75 dry wt% of wood, depending on process type and conditions (Furimsky 2000). Bio-oil, a dark brown viscous liquid, possesses a high oxygen content in the form of water and a complex mixture of numerous oxygenated chemical functionalities including carbonyl groups, acids, alcohols, aldehydes, esters, ketones, sugars, phenols, phenol derivatives, and a large proportion (20 to 30 wt%) of lignin derived oligomers (Marcelo et al., 2008). Moreover, it possesses relatively low heating value, low volatility, thermal instability, corrosiveness, immiscibility with fossil fuels and a tendency to polymerize over time, largely due to the presence of a high percentage of these reactive oxygenates (Zhang et al., 2006). The acids present in the bio-oil promote aldol reactions and also accelerate bio-oil aging (Diebold 2000).

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Raw bio-oils have been tested in diesel engines, turbines and Stirling engines. However, the results have been disappointing with objectionable engine erosion, deposits and significant wear except in Stirling engines. It is universally agreed that bio-oils must be substantially upgraded/deoxygenated prior to their utilization as engine fuels (Furimsky 2000, Wildschut et al., 2009, Senol et al., 2005). Presently, the widely employed bio-oil upgrading methods include hydrodeoxygenation (HDO) (Wildschut et al., 2009, De Miguel et al., 2010, Galdamez et al., 2005, Wang et al., 1996), catalytic cracking, super-critical treatment and steam reforming (Wang et al., 1996, Wang et al., 2000). Catalytic cracking can only partially deoxygenate the raw bio-oil and produces low liquid yields (Wang et al., 1996). Steam reforming produces a low energy density gaseous fuel and supercritical treatment requires high capital cost due to the requirement of high pressure vessels (Vadillo et al., 2013). Other upgrading methods such as olefination and esterification (Mahfud et al., 2007, Zhang et al., 2006) are used to upgrade bio-oil to boiler fuel.

Hydrodeoxygenation is one of the upgrading methods reported to produce a highly de-oxygenated (as low as zero wt% oxygen in the upgraded product), high energy liquid fuel. Previous hydrodeoxygenation studies (Elliot 2007, Elliot et al., 2009, Elliot et al., 2012) over nearly three decades have provided considerable information about methods to upgrade bio-oil by this technology. However, rapid catalyst deactivation (by coking), reactor plugging, and low product yields continue to be problematic and further research is required to refine current hydrodeoxygenation methods and catalysts. Our studies employed a pretreated bio-oil (PTBO) treated by HDO method to upgrade bio-oil to mixed liquid hydrocarbons. Moreover, instead of employing a two-step upgrading

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method (hydrotreatment followed by hydrocracking), a single-stage hydroprocessing was applied to produce liquid fuel from bio-oil.

It has become customary to practice the hydroprocessing of bio-oil by utilizing a 2-stage approach in which the 1st stage comprises a hydrotreating stage utilizing a mild temperature (<300 °C) for the reaction. This 1st stage eliminates the polymerization of bio-oil that occurs when raw bio-oil is subjected to high temperatures. Hydrocracking the hydrotreated product is then practiced in a 2nd stage reaction at higher temperature (>350 °C). The 2-stage hydroprocessing method usually requires 2 reactors which increases the capital cost of the hydroprocessing technology; more reaction time is also required increasing variable costs. The objective of this study was to apply a single-stage hydroprocessing treatment to upgrade a pretreated bio-oil (PTBO) to a hydrocarbon mixture.

4.3 Materials and Methods

4.3.1 Feedstock

PTBO was used as a feedstock for the hydrotreatment process. Raw bio-oil was produced using an augur pyrolysis reactor operated at a temperature between 400-550 °C. PTBO was produced by mixing the raw bio-oil. Following the addition of oxone and hydrogen peroxide the mixture was stirred for 90 min at room temperature and ambient pressure. Following this treatment the patent embodiment whereby butyric anhydride is added was performed for this study. For this step the mixture was heated at 90 °C at ambient pressure to obtain the final PTBO. A patent application has been filed to protect the intellectual property represented by the production of PTBO (Steele et al., 2011). The pretreatment step, unlike other bio-oil mild hydrotreating processes, was performed at

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low temperatures (below 100 °C) and at ambient pressure (no hydrogen pressure) in a Parr autoclave (450 mL) (Parr Instruments and Co).

4.3.2 Catalysts

CoMo/γ-Al_2O_3 and Ru/γ-Al_2O_3 were purchased commercially from Alfa Aesar and Acros Organics, respectively. Catalyst supports such as Si-Al, γ-alumina and the required inorganic metal salts for preparation of Ni/Si-Al and FeW/Si-Al catalysts were also commercially purchased. The Ni/Si-Al and FeW/Si-Al catalysts were prepared using the wet-impregnation method, whereby the metal salts were impregnated on catalyst supports and then dried at 120 °C for 4-6 hr before being calcined at 550 °C for 4 hr. The calcined metal-dispersed catalysts were then reduced at 700 °C using hydrogen flow (100 mLpm) for 4 hr. In case of 1:2 ratio of Ru/γ-Al_2O_3 and Ni/Si-Al catalyst, 1 ratio of Ru/γ-Al_2O_3 followed by 2 ratios of Ni/Si-Al catalyst was loaded in a separate heating zone. In the current study only reduced catalysts were tested. Reduced CoMo/γ-Al_2O_3 is considered a traditional hydrotreating catalyst. For all catalysts physical properties such as acid value (AV), water content (H_2O %), higher heating value (HHV) and oxygen content were compared. Based on the catalyst that performed the best in terms of physical properties, further tests on that catalyst will be performed. These tests were simulated distillation (SIMDIS) and detailed hydrocarbon analysis (DHA). The pressure drop for 8 hr of time on stream was measured in a packed-bed reactor as shown in Table 4.2.

4.3.3 Continuous packed-bed reactor

The continuous packed-bed reactor (Figure 4.1) used in the experiments consisted of a 1" I.D tubular reactor enclosed in a three-zone furnace (three 6" zones each

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independently controlled by its own temperature controller) followed by a condensation system. The temperatures inside the reactor were monitored with a point profile thermocouple equipped with ten sensing points (Omega Instruments). Three temperature sensing points were located in each of the 3 reactor heater zones for a total of 9. The tenth temperature sensing point was located at the condenser orifice. The catalyst bed temperature zones were maintained as closely as possible to the desired temperature set point through the course of the experiment. The catalytic reaction is exothermic such that temperatures are difficult to control due to the adiabatic nature of the reaction. Temperature controlled within a temperature range of 375-400 °C was possible. The bio-oil was pumped into the catalyst tube with a high pressure dual-pump system (Teledyne Isco 500D). The hydrogen flow rate was controlled with a mass flow controller (MFC; Brooks Instruments), and the reactor pressure was controlled with a back-pressure regulator. A schematic diagram of the reaction is shown in Figure 4.1.

For all experiments the reactor was loaded with catalyst at a temperature initially set to 150 °C. Figure 4.1 shows a diagram of the schematic of the continuous packed- bed reactor. Figure 4.2a and 4.2b shows the method of catalyst loading in the continuous packed-bed reactor. Once this initial temperature set point was attained, the reactor temperature was raised by another 100 °C upon reaching the resultant temperature of 250 °C and the reactor temperature was again raised to 350 °C. A final 25 to 50 °C increase was often applied to raise the actual reaction temperature as close to 375 °C as possible. The reactor was pressurized to the desired 1500 psi hydrogen reaction pressure. After attaining the temperature of approximately to 375 °C, the desired pressure of 1000 psi

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hydrogen was supplied to the reactor by a mass flow controller (MFC) producing a desired flow rate of 500 ml/min.

All experiments were performed at a LHSV of 0.2 to 0.3 h^{-1}. The exit gas flow rate in milliliters per minute (ml/min) was monitored by an Agilent gas flow meter. Products exiting from the packed-bed reactor were cooled in the condenser and the liquid products were collected in a sampling bottle at 2 h intervals. Periodic gas sampling was also performed every 2 h using Tedlar sampling bags. The collected liquid products were centrifuged for 1 h to separate the aqueous fraction (AF) and organic fraction (OF). The experiments were performed over a period of 8 h. Table 4.1 describes the numbered components of the continuous packed-bed reactor provided in Figure 4.1, Figure 4.2a and Figure 4.2b. Figure 4.2. shows the method of catalyst loading in the continuous packed-bed reactor (a. Method of catalyst loading inside the reactor, enclosed in a furnace; b. Inside reactor with loaded catalyst).

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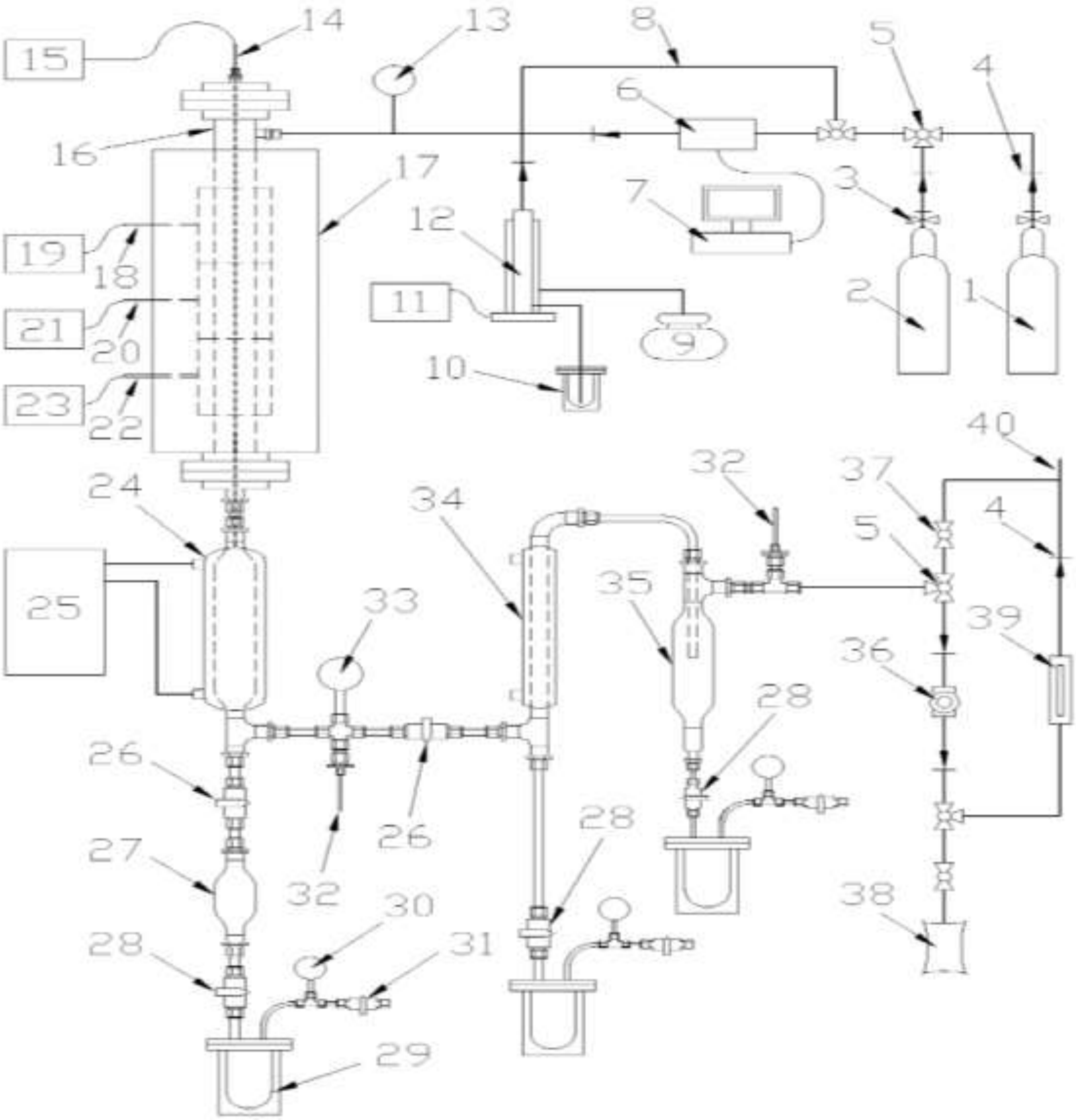

Figure 4.1 Schematic of the continuous packed-bed reactor.

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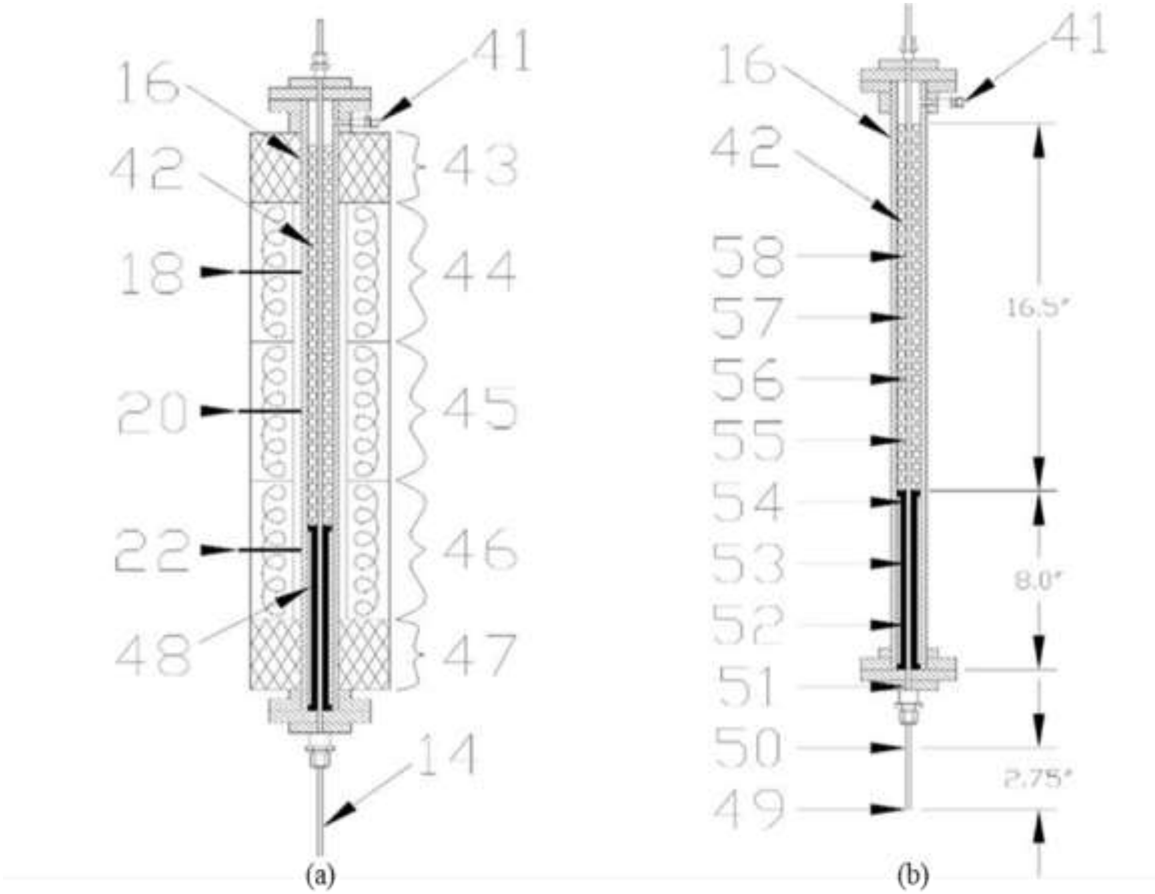

Figure 4.2 Method of catalyst loading in continuous packed-bed reactor

(a. Method of catalyst loading inside the reactor, enclosed in a furnace; b. Inside reactor with loaded catalyst).

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Table 4.1 The numbered components of the continuous packed-bed reactor provided in Figure 4.1 and Figure 4.2 (4.2a and b).

1	Hydrogen cylinder	30	Sampling vessel pressure gauge
2	Air cylinder	31	Sampling vessel ball valve
3	Cylinder regulator	32	Thermocouple
4	Check valve	33	Reactor exit pressure gauge
5	Three-way valve	34	Condenser 2
6	Mass flow controller (MFC)	35	Condenser 3
7	Computer-MFC program	36	Back pressure regulator
8	MFC bypass line	37	Needle valve
9	Air compressor	38	Gas sample bag
10	Bio-oil	39	Exit gas flow meter
11	High pressure pump controller	40	Gas exit line
12	High pressure pump	41	Bio-oil inlet
13	Reactor inlet pressure gauge	42	Catalyst
14	Ten zone reactor thermocouple	43	Heater top insulation, 3” long
15	Ten zone thermocouple monitor	44	Heater zone 1, 6” long
16	Reactor tube	45	Heater zone 2, 6” long
17	Reactor tube heater	46	Heater zone 3, 6” long
18	Heater zone 1 thermocouple	47	Heater bottom insulation, 3” long
19	Heater zone 1 controller	48	Catalyst support
20	Heater zone 2 thermocouple	49	Reactor thermocouple zone 1
21	Heater zone 2 controller	50	Reactor thermocouple zone 2
22	Heater zone 3 thermocouple	51	Reactor thermocouple zone 3
23	Heater zone 3 controller	52	Reactor thermocouple zone 4
24	Condenser 1	53	Reactor thermocouple zone 5
25	Chiller	54	Reactor thermocouple zone 6
26	Ball valve	55	Reactor thermocouple zone 7
27	Hydrocarbons storage vessel	56	Reactor thermocouple zone 8
28	Needle valve	57	Reactor thermocouple zone 9
29	Sampling vessel	58	Reactor thermocouple zone 10

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4.4 Physical and chemical analysis

PTBO and the liquid products produced from the HDO treatments were analyzed for acid value (AV), water content (H_2O %), higher heating value (HHV), elemental analysis and GC-MS analysis. AV was obtained by dissolving one gram of bio-oil in an isopropanol/water mixture and titrating to a pH of 8.5 with 0.1 N KOH by ASTM D 664. Percent water was determined by ASTM Method E 203 with a Cole-Parmer Model C-25800-10 titration apparatus. The HHV was determined with a Parr 6400 automatic isoperibol calorimeter by ASTM D 240. Elemental analyses of raw bio-oil were performed with an EA920 elemental analyzer by ASTM D 5291. Detailed hydrocarbon analysis (DHA) was performed using ASTM D6730-01 method. DHA was performed in the PerkinElmer Clarus 680 GC equipped with a built-in model Arnel 4060 Detailed Hydrocarbon Analyzer. Simulated distillation was performed by the ASTM D2887 method on a gas chromatograph.

4.5 Results and Discussion

Our study focused on testing the efficacy of various catalysts in single-stage hydroprocessing of PTBO to liquid hydrocarbons. The catalysts employed for this study included FeW/Si-Al, CoMo/γ-Al_2O_3, iron oxide-chromium oxide (Fe-Cr) catalyst, and 1:2 ratio of Ru/γ-Al_2O_3: Ni/Si-Al. The collected liquid products were centrifuged for 1 hr to separate the aqueous and hydrocarbon fractions. The hydrocarbon fractions of the liquid products were subjected to characterizations such as elemental analysis, HHV, AV, and H_2O% analysis to determine quality, based on which the catalyst performance was interpreted. The reduction in AV, increase in HHV accompanied by decreased elemental oxygen in the hydrocarbon fraction of the product indicated reduction of bio-oil oxygen.

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The pressure drop values were measured with time on stream for 8 hr in a packed-bed reactor as shown in Table 4.2.

Table 4.2 Effect of pressure drop of packed-bed reactor by catalyst applied with time on stream.

Catalyst	Pressure difference (psi)	Time (hrs)
FeW/Si-Al	3	2
	3	4
	4	6
	4	8
CoMo/ γ-Al_2O_3	3	2
	3	4
	4	6
	4	8
Fe-Cr mixed oxide	3	2
	2	4
	4	6
	5	8
1:2 ratio of Ru/γ-Al_2O_3 and Ni/Si-Al	2	2
	3	4
	4	6
	3	8

Table 4.3 Hydrotreating catalysts, experimental conditions applied and properties

Catalyst	Temperature (°C)	P (Psig)	LHSV (h^{-1})	AV	HHV	H_2O%
Control-Pretreated bio-oil (PTBO)				223.0	19.0	21.0
FeW/Si-Al	300-375	1500	0.2-0.3	51.9	33.0	7.6
CoMo/γ-Al_2O_3				2.1	43.1	0.2
Fe-Cr mixed oxide				24.8	35.4	4.9
1:2 ratio of Ru/γ-Al_2O_3 and Ni/Si-Al				16.5	41.6	0.3

(AV, HHV, H_2O%) of the hydrocarbon fraction of the liquid products.

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Table 4.4 The elemental analysis of the hydrocarbon fraction produced by catalyst type.

Catalyst	%C	$\%H_2$	$\%N_2$	$\%O_2$ (100 -%C+$\%H_2$ +$\%N_2$)
PTBO	43.1	8.9	0.2	47.8
FeW/Si-Al	81.7	10.0	0.4	7.9
CoMo/γ-Al_2O_3	86.3	13.4	0.4	0.1
Fe-Cr mixed oxide	69.1	11.2	0.2	19.5
1:2 ratio of Ru/γ-Al_2O_3 and Ni/ Si-Al	85.5	13.8	0.1	0.6

Table 4.5 Effect of catalyst type on total liquid, organic fraction (OF) and aqueous fraction (AF) yields (based on dry weight of biomass).

Catalyst	Yields (g/g of feed)		
	Total liquid	HF	AF
FeW/Si-Al	0.34	0.05	0.29
CoMo/ γ-Al_2O_3	0.34	0.02	0.32
Fe-Cr mixed oxide	0.44	0.10	0.34
1:2 ratio of Ru/γ-Al_2O_3 and Ni/Si-Al	0.47	0.14	0.33

Results were compared between the control sample (PTBO) and the hydrocarbon liquid fractions from catalytic hydroprocessing experiments using catalysts FeW/Si-Al, CoMo/γ-Al_2O_3, Fe-Cr mixed oxide catalyst, and 1:2 ratio of Ru/γ-Al_2O_3, Ni/Si-Al. Applying these catalysts to the PTBO hydroprocessing produced respective AV's of 51.9, 2.1, 24.8 and 16.5 mg of KOH/g oil. As evident from Table 4.2, all the catalysts significantly decreased the AV, with CoMo/γ-Al_2O_3 being the most effective catalyst. HHVs produced by these catalysts were 33.0, 43.1, 35.4 and 41.6 MJ/kg, respectively. Table 4.4 shows the elemental oxygen in the liquid products obtained using the above mentioned catalysts were 7.9%, 0.06%, 19.5%, and 0.6%, respectively. The best results

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in terms of AV, HHV, H_2O%, and elemental oxygen obtained using the CoMo/γ-Al_2O_3 catalyst were 2.1, 43.1, 0.2 and 0.06%, respectively. The best experiments showing best results were repeated for 3 times.

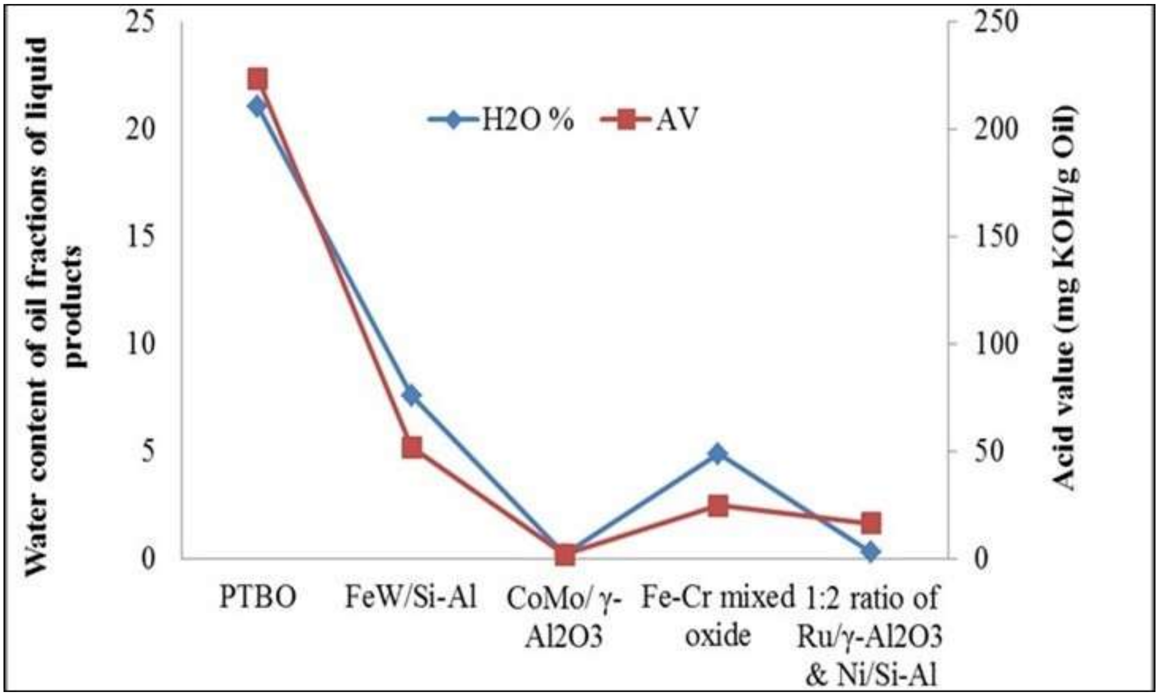

Figure 4.3 Effect of catalysts on H_2O% of the liquid products.

All liquid products obtained from the HDO experiments contained two (aqueous and hydrocarbon) fractions. Figure 4.3, showing the H_2O% content of the hydrocarbon fractions, indicated that the CoMo/γ-Al_2O_3 resulted in the formation of a hydrocarbon fraction with negligible (0.2%) water content. The 1:2 ratio of Ru/γ-Al_2O_3 and Ni/Si-Al, and Fe-Cr, FeW upgraded hydrocarbon fractions showed 0.3, 4.9 and 7.6% with respective water contents. Figure 4.3 shows an increase in AV followed by the trend of increasing water content.

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Figure 4.4 shows the effect of hydrotreating catalysts in increasing the HHV of the hydrocarbon fractions. All hydrocarbon fractions showed increased HHVs compared to the PTBO. While CoMo/γ-Al_2O_3 was the most effective catalyst in improving the HHV of the hydrocarbon fraction (~43.0 MJ/Kg), 1:2 ratio of Ru/γ-Al_2O_3, Ni/Si-Al was also effective in increasing the HHV (~42.0 MJ/kg). From Figures 4.4 and 4.5 it can be determined that the increase in HHV of the hydrocarbon fractions was a function of the decrease in the water content and AVs.

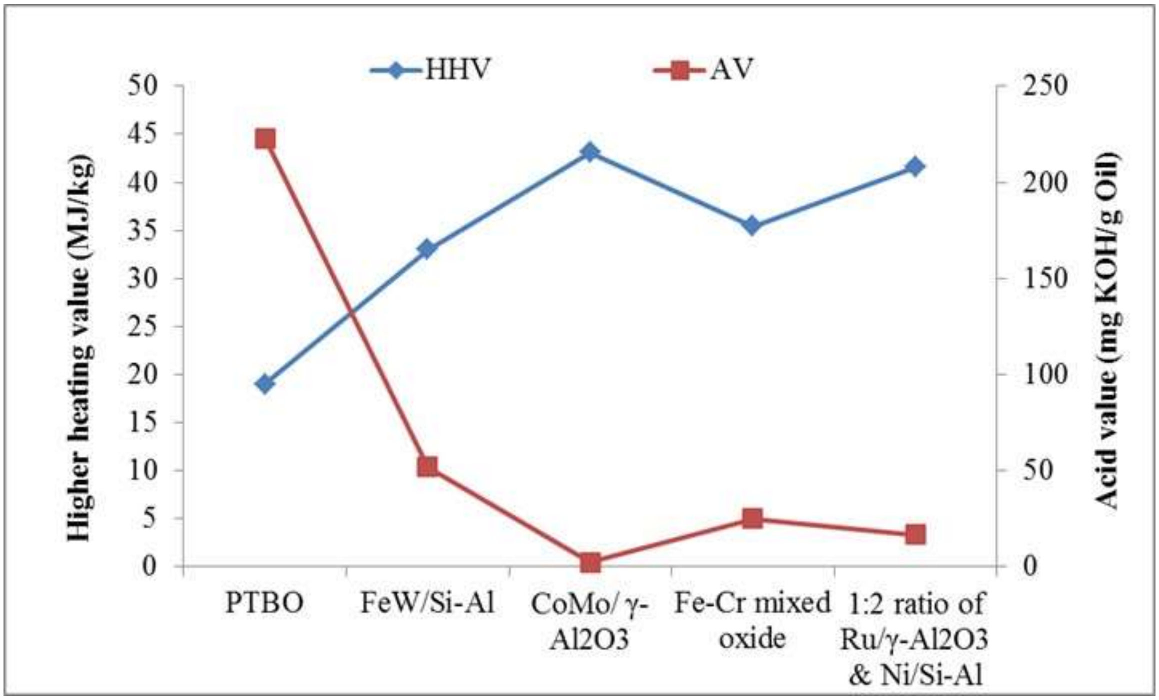

Figure 4.4 Effect of catalysts on AV and HHV of the liquid products.

As shown in Table 4.5, the total yields produced by FeW/Si-Al, CoMo/γ-Al_2O_3, Fe-Cr mixed oxide and 1:2 ratio of Ru/γ-Al_2O_3 and Ni/Si-Al catalyst were 0.34, 0.34, 0.44, 0.47 g/g of feed, respectively, for a time on stream of 8 hrs. Among the tested

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catalysts, the highest oil yields were produced by Fe-Cr mixed oxide catalyst and 1:2 ratio of Ru/γ-Al_2O_3, Ni/Si-Al catalysts, but the overall quality of the product deteriorated over time with these catalysts. Though the total oil yields were less with CoMo/γ-Al_2O_3 catalyst, the quality/properties of the product obtained after 8 hr were similar to that of the product obtained after the initial run.

4.6 Analysis

4.6.1 DHA Analysis

Table 4.6 gives the detailed hydrocarbon analysis (DHA) of mixed liquid hydrocarbons obtained with CoMo/γ-Al_2O_3 and 1:2 ratio of Ru/γ-Al_2O_3, Ni/Si-Al catalyst. For the reduced CoMo/γ-Al_2O_3 catalyst, the olefins, iso-paraffins, and C14+ compounds dominated the mixed liquid hydrocarbons followed by naphthenes and aromatics with an octane value of 52.3 on an average of three replicates. In comparison, the detailed hydrocarbon analysis of the 1:2 ratio of Ru/γ-Al_2O_3, Ni/Si-Al catalyst upgraded product predominantly contained iso-paraffins, olefins and aromatics over C14+ compounds, naphthenes and iso-paraffins with an octane value of 50.2 on an average of three replicates.

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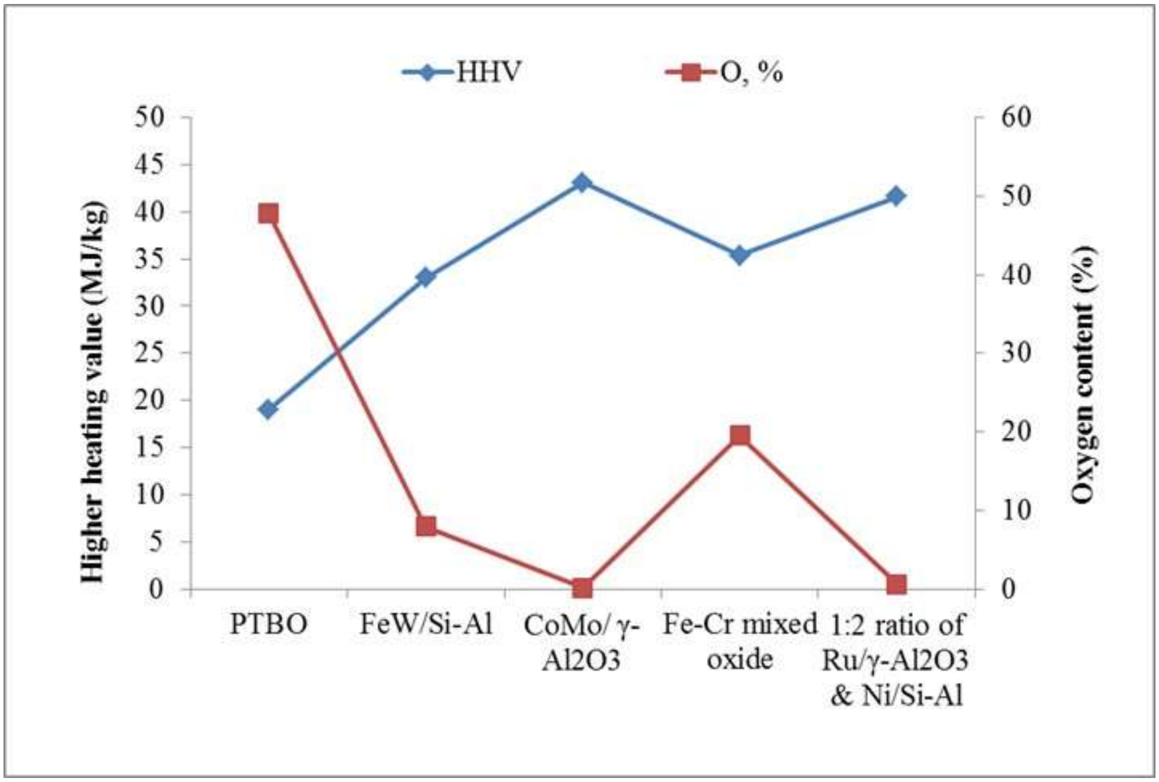

Figure 4.5 Elemental oxygen in the liquid products obtained on hydroprocessing.

Table 4.6 DHA mass percentage of CoMo/γ-Al_2O_3 and 1:2 ratio of Ru/γ-Al_2O_3 and Ni/Si-Al upgraded oil fractions (ASTM D6730-01).

Catalyst	CoMo/γ-Al_2O_3	1:2 ratio of Ru/γ-Al_2O_3 and Ni/Si-Al
Paraffins	2.98	0.45
I-Paraffins	18.19	23.90
Olefins	17.51	14.83
Naphthenes	14.18	9.45
Aromatics	7.97	11.22
Total C14+	13	10.90
Unknowns	25.58	28.19
Octane #	52.33	50.20

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4.6.2 Gas analysis

Table 4.7 shows the analysis of gas samples collected during the hydroprocessing experiments. Gas samples were collected 10-15 minutes prior to collecting the liquid samples. Gas analysis was used to interpret the H_2 percentage in the exit gas as well as the formation of low molecular weight hydrocarbon gases such as CH_4, C_2H_6, etc. As seen below in Table 4.7, exit gases from the CoMo/γ-Al_2O_3 experiment contained the lowest hydrogen percentage, indicating that more hydrogen was consumed for hydroprocessing PTBO. This observation is in agreement with the elemental analysis results that showed the presence of 13.4% hydrogen in the CoMo/γ-Al_2O_3 upgraded oil fraction compared to 10.6% and 11.2 % hydrogen present in the FeW/ Si-Al and Fe-Cr mixed oxide upgraded hydrocarbon fractions. The exit gases from the experiment using Ru/γ-Al_2O_3 and Ni/Si-Al catalyst combination had 74.0% hydrogen which had the next best performance to the CoMo/ γ-Al_2O_3 gas samples.

Table 4.7 Gas analysis results from hydroprocessing experiments by catalyst type.

Catalyst	H_2%	O_2%	N_2%	CH_4%	CO%	CO_2%	C_2H_6%
FeW/Si-Al	79.21	0.41	1.36	0.06	0.44	1.01	0.02
CoMo/γ-Al_2O_3	69.79	0.25	0.72	5.73	0.16	1.66	0.93
Fe-Cr	81.74	0.48	1.5	0.25	0	1.84	0.06
Ru/ γ-Al_2O_3 + Ni/Si-Al	74.38	0.15	0.38	7.23	0	0.36	0.29

4.6.3 SIMDIS

Simulated distillation (SIMDIS) was perfomed according to ASTM D2887 method on the CoMo/γ-Al_2O_3 upgraded liquid fuel and the plot is shown in Figure 4.6. Simulated distillation of the fuel showed IBP (Initial Boiling Point) and FBP (Final

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Boiling Point) to be 69 °C and 304 °C, respectively. Therefore, it can be reported that the obtained liquid fuel may have a boiling temperature range of 69 to 304 °C and contain petroleum equivalents of 50% gasoline (38-170 °C), 30% jet fuel (170-250 °C) and 20% diesel (250-304 °C) range hydrocarbons. Simulated distillation showed no presence of vacuum gas oil (VGO) range (> 315 °C) hydrocarbons in our fuel.

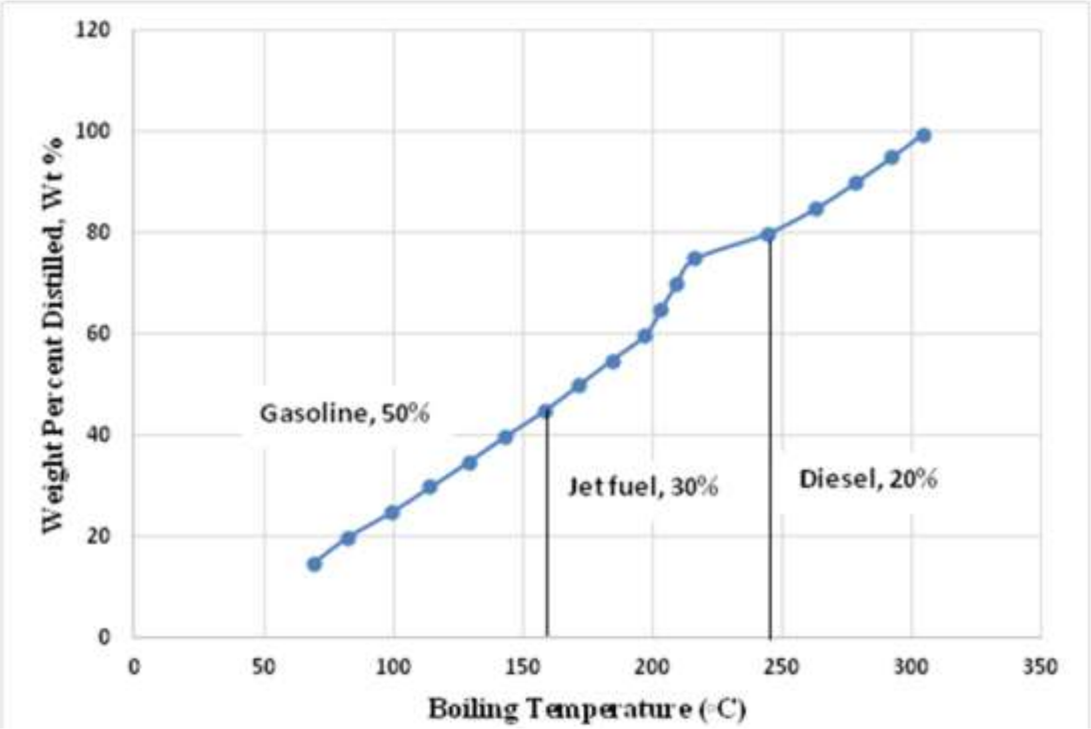

Figure 4.6 Wt% distilled vs boiling temperature T_b (°C) of the CoMo/γ-Al_2O_3 upgraded liquid fuel determined by simulated distillation GC (ASTM D2887).

4.7 Conclusion

This research successfully demonstrated that PTBO can be hydrotreated to a 100% hydrocarbon mixture utilizing only single-stage hydroprocessing (hydrotreating and hydrocracking) in a packed-bed reactor. Among the catalysts tested for this single-

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stage experiment the best results were obtained using reduced CoMo/γ-Al_2O_3 catalyst for hydrotreating the PTBO at 350-400 °C with a hydrogen flow rate of 0.5 L/min at 1500 Psig H_2 pressure and an LHSV of 0.2-0.3 h^{-1}. The obtained liquid fuel had an AV of 2.1 with a heating value of 43.1 MJ/Kg, elemental oxygen of 0.06% and water content of 0.18%. Gas analysis results indicated that the reduced CoMo/γ-Al_2O_3 catalyst had the highest hydrogen consumption among all the catalysts. Simulated distillation results showed that our liquid fuel contained petroleum equivalents of 50% gasoline (38-170 °C), 30% jet fuel (170-250 °C) and 20% diesel (250-304 °C) range hydrocarbons. The high activity of promoted Mo catalyst (CoMo/γ-Al_2O_3) can be attributed to the availability of number of "d" electrons in the highest occupied orbitals. The promoter element (Co) aids in reducing the oxidation state of the Mo atom by donating electrons to Mo atoms and thereby increasing the number of 4d electrons.

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CHAPTER V

COMPARISON OF REDUCED AND SULFIDED COMO/γ-Al_2O_3 CATALYST ON HYDROPROCESSING OF PRETREATED BIO-OIL AND COMPARISON OF HYDROPROCESSED PRODUCT FROM BIO-OIL AND PRETREATED BIO-OIL IN A CONTINUOUS PACKED-BED REACTOR

5.1 Abstract

Pretreated bio-oil was hydroprocessed with conventional sulfided CoMo/γ-Al_2O_3 catalyst in a continuous packed-bed reactor. Hydroprocessing experiments were performed at a temperature of 350-400 °C, 1500 psig hydrogen pressure, using a hydrogen flow rate of 500 ml/min at a liquid hourly space velocity of 0.2 h^{-1}. The results from sulfided catalytic experiments were compared to our prior studies on hydroprocessing pretreated bio-oil with reduced CoMo/γ-Al_2O_3 catalyst. Sulfided CoMo/γ-Al_2O_3 catalyst demonstrated higher catalytic activity and resulted in increased hydrocarbon fraction yields. Moreover, the quality of the hydrocarbon fraction, as determined by the acid value, higher heating value, and water content analysis, also improved. Sulfided CoMo/γ-Al_2O_3 catalyst produced a hydrocarbon fraction having a higher heating value of 44.4 MJ/kg, acid value of 0.5 mg KOH/g oil, and a total water content of 0.1%. Use of sulfided catalyst for hydroprocessing pretreated bio-oil decreased the oxygen content from 47.8 wt% in the pretreated bio-oil to non-detectable limits (~0

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wt%) in the hydrocarbon fraction. The hydrocarbon fraction was also analyzed by detailed hydrocarbon analysis and simulated distillation.

5.2 Introduction

Biomass, due to its carbon value, abundance, and renewability, is an attractive resource for the production of fuels as well as value-added chemicals. Lignocellulosic biomass has negligible sulfur, nitrogen and inorganic content and is also considered CO_2 neutral (Sharma et al., 1993). Fast pyrolysis of biomass is a thermochemical process performed at 400-500 ^oC in the absence of oxygen, produces bio-oil (60-75 wt%), solid char (15-25 wt%) and non-condensable gases (10-20 wt%); product distribution depends on the type of feedstock and process conditions employed (Mohan et al., 2006). Bio-oil is a complex mixture containing numerous oxygenates in the form of a wide range of functional groups, including alcohols, aldehydes, ketones, ethers, esters, acids and others. These numerous oxygenated compounds result in 45-50 wt% oxygen content, water is the most abundant oxygenated compound as it typically ranges between 25 to 30 wt% (Mohan et al., 2006).

Bio-oil is a viscous and highly acidic liquid product with a pH typically ranging between 2.5 to 3.0, with a low heating value (~17 MJ/Kg). Moreover, the presence of reactive oxygenates make bio-oil thermodynamically unstable and, upon storage, causes phase separation due to polymerization reactions (Mohan et al., 2006, Czernik and Bridgwater 2004, Ozbay et al., 2006). Despite its disadvantages, bio-oils have been tested as boiler fuel for stationary power and heat production, for chemical extraction, and also tested as engine fuels. However, the oxygenated bio-oils invariably caused engine damage regardless of the engine type tested (Bridgwater 1999). Therefore, bio-oil, to be

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utilized as a transportation fuel, must be upgraded to a stable hydrocarbon liquid (Mohan et al., 2006, Furimsky 2000, Elliot 2007).

A number of upgrading methods have been proposed to improve the bio-oil quality, physical and chemical properties and to produce high-quality fuels from bio-oils. All depend on oxygen removal in one way or another. The upgrading methods include catalytic hydroprocessing (Elliot 2007), esterification (Tang et al., 2008, Xu et al., 2010, Xiong et al., 2009), olefination (Zhang et al., 2011, Zhang et al., 2013, Chatterjee et al., 2013), catalytic pyrolysis (French et al., 2010, Aho et al., 2007), hydrodeoxygenation (HDO) (Elliot 2007, wildschut et al., 2009, Senol et al., 2005), steam reforming (Wang et al., 1996, Galdamez et al., 2005), decarbonylation and decarboxylation (Mortensen et al., 2011). Hydrodeoxygenation (HDO) has been studied extensively for conversion of bio-oil to liquid hydrocarbons.

Elliot et al. developed a two-step hydrotreating process for upgrading of pyrolysis oil which was characterized by a low temperature mild hydrotreating step, performed at a temperature of 270 °C and 13.6 MPa pressure to avoid polymerization of oxygen-containing compounds, catalyst coking and reactor plugging. This hydrotreating step was then followed by a higher temperature hydrocracking performed at 400 °C and 13.6 MPa pressure to remove oxygen in the presence of sulfided (CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3) catalysts. This process of low temperature hydrotreating followed by hydrocracking is now widely used by many HDO practioners. Sulfided CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3 catalysts have been studied extensively for HDO, due to their success in deoxygenating and cracking of pyrolysis oils (Elliot et al., 2007, Elliot et al., 1996,

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Elliot et al., 1988, Elliot and Oasmaa 1991, Mahfud 2007, Senol 2007, Gutierrez et al., 2007).

Pacific Northwest National Laboratory (PNNL) researchers initially performed tests on biomass liquefaction products rather than fast pyrolysis bio-oil and screened 22 catalysts to determine their performance. The PNNL researchers observed that the sulfided forms of the CoMo and NiMo catalysts are more active than the oxide form (Elliot 2007). The CoMo and NiMo catalysts are more active in the sulfided form than in the non-sulfided form. Therefore, the catalysts are either presulfided with a sulfiding agent or sulfided on stream by the addition of a sulfiding agent to the feed. The sulfiding agent can be either hydrogen sulfide or a carbon containing sulfur compound (Senol 2007).

The relatively higher activity of sulfided CoMo or NiMo/γ-Al_2O_3 can be attributed to the formation of the active Co(Ni)MoS phase, consisting of highly dispersed MoS_2 crystallites coated with Co or Ni atoms that act as promoters when the oxide form was subjected to sulfidation process (Nikulshin et al., 2014). Sulfidation changes the surface structure of the catalyst, and creates active sites with various configurational and energetic properties. It is generally agreed that sulfur anion vacancies (coordinatively unsaturated sites), located at the edge of MoS_2 nanoclusters are the catalytic sites formed in the presence of a sulfiding agent and hydrogen. These sites show lewis acid character, and they can adsorb atoms with unpaired electrons. Thus, the sulfur anion vacancies can play a role in the rupture of carbon-heteroatom bonds (Senol 2007).

Xu et al. (2011) performed oxidation of raw bio-oil via ozone pretreatment to convert aldehydes to acids. Parapati et al. (2014) and Steele et al. (2013) have described

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the production of pretreated bio-oil (PTBO) from oxidation of raw bio-oil. Parapati et al. (2014) tested one embodiment of the Steele et al. (2013) patent by oxidizing raw bio-oil with 3 wt% oxone combined with 10 wt% hydrogen peroxide with a final addition of 25 wt% of butyric anhydride. Steele et al. (2013) demonstrated that the PTBO allowed hydrotreating raw bio-oil with syngas. Parapati et al. (2014) performed hydroprocessing of PTBO with four different catalysts with 100% pressurized hydrogen gas and determined that reduced CoMo/γ-Al_2O_3 produced the best hydrocarbon properties. However, the reduced CoMo/γ-Al_2O_3 yield was low at only 0.02 g/g of feed (based on dry weight of biomass) (Parapati et al., 2014).

The intent of our current research was to improve the yields and products possible from hydroprocessing of PTBO whereby hydroprocessing catalysis with sulfided CoMo/γ-Al_2O_3 were compared to reduced CoMo/γ-Al_2O_3 with respect to yield and physical and chemical properties. The sulfided CoMo/γ-Al_2O_3 catalyst was employed for single-stage hydroprocessing of PTBO in this study. Process conditions included a temperature of 350-400 °C, 1500 psig hydrogen pressure, hydrogen flow rate (HFR) of 500 ml/min and a liquid hourly space velocity (LHSV) of 0.2 h^{-1}.

5.3 Experimental

5.3.1 Materials

Oxone, hydrogen peroxide (H_2O_2) 30 wt% solution in water and butyric anhydride were purchased commercially from Sigma-Aldrich. CoMo/γ-Al_2O_3 was purchased from Alfa Aesar. Cyclohexane and carbondisulfide were purchased from Fisher Scientific. The oxide form of catalysts was activated by subjecting them to a sulfidation process prior to hydroprocessing experiments. CoMo/γ-Al_2O_3 was sulfided

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with a solvent mixture of 2 vol % carbon disulfide and cyclohexane. To 800 ml of cyclohexane solvent, 16 ml (2 vol %) of carbon disulfide was added and the solvent mixture was pumped through a high-pressure dual-pump system. Sulfiding of the catalyst was performed at 300 °C, a pressure of 750 psi and LHSV of 1 h^{-1} for a period of 4 hrs. Bio-oil (RBO) was produced by the fast pyrolysis process at a temperature of 400-450 °C under nitrogen gas atmosphere using a 7 kg/h auger-fed pyrolysis reactor located in the Department of Sustainable Bioproducts, Mississippi State University.

5.3.2 Methods

5.3.2.1 Pretreatment of bio-oil

The pretreatment (oxidation) of raw bio-oil was performed at ambient temperature and pressure in a Parr autoclave (450 ml) equipped with an electronic stirrer. Bio-oil oxidation was performed by the addition of 3 wt% oxone and 10 wt% H_2O_2 and the mixture was stirred for 90 min at room temperature. Following this step, 25 wt% butyric anhydride was added and the reaction mixture and was stirred for 90 min at 90 °C to obtain the final experimental PTBO.

5.3.3 Continuous packed-bed reactor

The continuous packed-bed reactor (Figure 4.1) used in the experiments consisted of a 1" I.D tubular reactor enclosed in a three-zone furnace (three 6" zones each independently controlled by its own temperature controller) followed by a condensation system. The temperatures inside the reactor were monitored with a point profile thermocouple equipped with ten sensing points (Omega Instruments). Three temperature sensing points were located in each of the 3 reactor heater zones for a total of 9. The tenth

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temperature sensing point was located at the condenser orifice. The catalyst bed temperature zones were maintained as closely as possible to the desired temperature set point through the course of the experiment. The catalytic reaction is exothermic such that temperatures are difficult to control due to the adiabatic nature of the reaction. Temperature controlled within a temperature range of 375-400 °C was possible. The bio-oil was pumped into the catalyst tube with a high pressure dual-pump system (Teledyne Isco 500D). The hydrogen flow rate was controlled with a mass flow controller (MFC; Brooks Instruments), and the reactor pressure was controlled with a back-pressure regulator. A schematic diagram of the reaction is shown in Figure 5.1.

For all experiments the reactor was loaded with catalyst at a temperature initially set to 150 °C. Figure 5.1 shows a diagram of the schematic of the continuous packed- bed reactor. Figure 5.2a and 5.2b shows the method of catalyst loading in the continuous packed-bed reactor. Once this initial temperature set point was attained, the reactor temperature was raised by another 100 °C upon reaching the resultant temperature of 250 ^{o}C and the reactor temperature was again raised to 350 °C. A final 25 to 50 ^{o}C increase was often applied to raise the actual reaction temperature as close to 375 ^{o}C as possible. The reactor was pressurized to the desired 1500 psi hydrogen reaction pressure. After attaining the temperature of approximately 375 ^{o}C, the desired pressure of 1000 psi hydrogen was supplied to the reactor by a mass flow controller (MFC) producing a desired flow rate of 500 ml/min.

All experiments were performed at a LHSV of 0.2 h^{-1}. The exit gas flow rate in milliliters per minute (ml/min) was monitored by an Agilent gas flow meter. Products exiting from the packed-bed reactor were cooled in the condenser and the liquid products

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were collected in a sampling bottle at 2 h intervals. Periodic gas sampling was also performed every 2 h using Tedlar sampling bags. The collected liquid products were centrifuged for 1 h to separate the aqueous fraction (AF) and organic fraction (OF). The experiments were performed over a period of 8 h. Table 5.1 describes the numbered components of the continuous packed-bed reactor provided in Figure 5.1, Figure 5.2a and Figure 5.2b. Figure 5.2. shows the method of catalyst loading in the continuous packed-bed reactor (a. Method of catalyst loading inside the reactor, enclosed in a furnace; b. Inside reactor with loaded catalyst). The experiments showing best results were repeated for 3 times.

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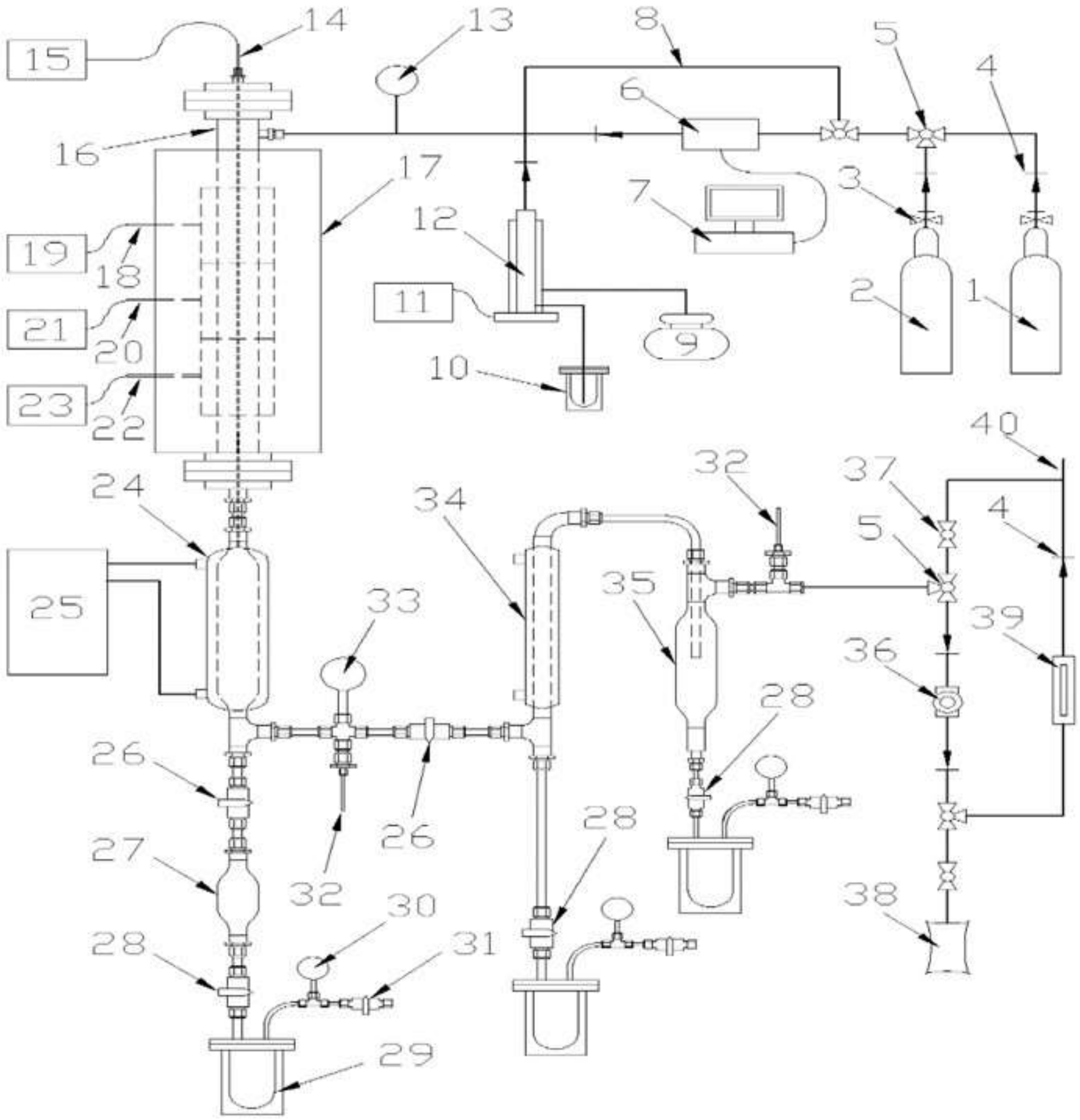

Figure 5.1 Schematic of the continuous packed-bed reactor.

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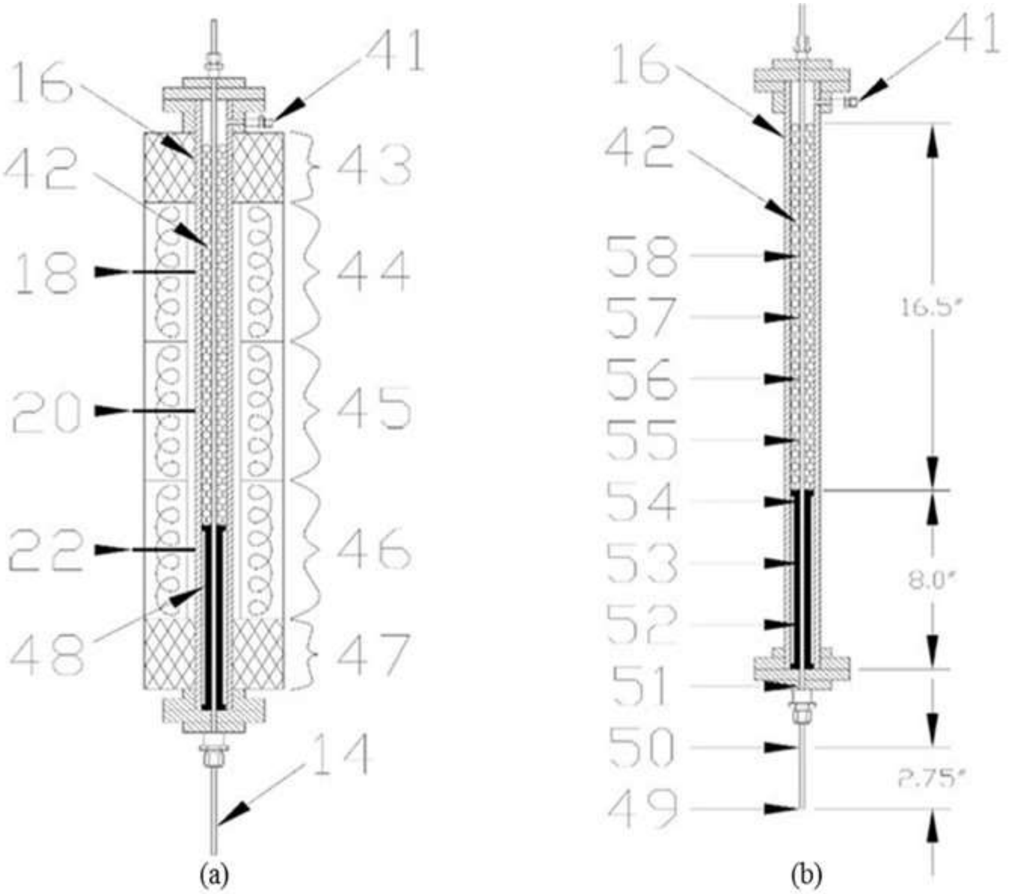

Figure 5.2 Method of catalyst loading in continuous packed-bed reactor

(a. Method of catalyst loading inside the reactor, enclosed in a furnace; b. Inside reactor with loaded catalyst).

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Table 5.1 The numbered components of the continuous packed-bed reactor provided in Figure 5.1 and Figure 5.2 (5.2a and b).

1	Hydrogen cylinder	30	Sampling vessel pressure gauge
2	Air cylinder	31	Sampling vessel ball valve
3	Cylinder regulator	32	Thermocouple
4	Check valve	33	Reactor exit pressure gauge
5	Three-way valve	34	Condenser 2
6	Mass flow controller (MFC)	35	Condenser 3
7	Computer-MFC program	36	Back pressure regulator
8	MFC bypass line	37	Needle valve
9	Air compressor	38	Gas sample bag
10	Bio-oil	39	Exit gas flow meter
11	High pressure pump controller	40	Gas exit line
12	High pressure pump	41	Bio-oil inlet
13	Reactor inlet pressure gauge	42	Catalyst
14	Ten zone reactor thermocouple	43	Heater top insulation, 3” long
15	Ten zone thermocouple monitor	44	Heater zone 1, 6” long
16	Reactor tube	45	Heater zone 2, 6” long
17	Reactor tube heater	46	Heater zone 3, 6” long
18	Heater zone 1 thermocouple	47	Heater bottom insulation, 3” long
19	Heater zone 1 controller	48	Catalyst support
20	Heater zone 2 thermocouple	49	Reactor thermocouple zone 1
21	Heater zone 2 controller	50	Reactor thermocouple zone 2
22	Heater zone 3 thermocouple	51	Reactor thermocouple zone 3
23	Heater zone 3 controller	52	Reactor thermocouple zone 4
24	Condenser 1	53	Reactor thermocouple zone 5
25	Chiller	54	Reactor thermocouple zone 6
26	Ball valve	55	Reactor thermocouple zone 7
27	Hydrocarbons storage vessel	56	Reactor thermocouple zone 8
28	Needle valve	57	Reactor thermocouple zone 9
29	Sampling vessel	58	Reactor thermocouple zone 10

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5.4 Physical and chemical analysis

PTBO and the OF produced from the hydroprocessing treatments were characterized following ASTM methods. For the AV test, 1 g of sample was dissolved in isopropanol/water (v/v =35:65) solution and then titrated with 0.1 N NaOH to a pH of 8.5. The AV was then calculated as the required milligrams (mg) amounts of NaOH equivalent to 1 g of sample, according to ASTM D664. The HHV was determined with a Parr 6400 automatic isoperibol calorimeter according to ASTM D240. The Karl Fischer method was employed to determine water content by ASTM E203 with a Cole-Parmer Model C-25800-10 titration apparatus. Elemental analysis (CHNO) for determination of percent carbon (C) percent hydrogen (H), percent nitrogen (N) and percent oxygen (O) were determined by EAI CE-440 elemental analyzer, with oxygen content determined by difference by the ASTM D5291 method. The best-performing catalysts were selected based on lowest O content in their deoxygenated products. Product analysis was by detailed hydrocarbon analysis (DHA) and simulated distillation (SIMDIS). DHA was performed by a PerkinElmer Clarus 680 GC equipped with a built-in model Arnel 4060 DHA analyzer, performed by ASTM D6730-01 method. SIMDIS was performed by the ASTM D2887 method on a gas chromatograph.

5.5 Results and Discussion

5.5.1 Comparison of reduced and sulfided CoMo/γ-Al_2O_3 catalyst on hydroprocessing

Table 5.2 shows the properties of OF obtained by the hydroprocessing of the PTBO. The reduced CoMo/γ-Al_2O_3 data was adapted from Parapati et al. (2014). The properties of the PTBO control are shown in Table 5.2 to allow comparison with the

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properties of OF's obtained with reduced CoMo/γ-Al_2O_3 and sulfided CoMo/γ-Al_2O_3 catalysts. Table 5.2 indicates that after hydroprocessing of PTBO with the reduced CoMo/γ-Al_2O_3 and sulfided CoMo/γ-Al_2O_3 catalyst, the AV decreased from 241.0 of PTBO to 2.1 and 0.5 mg KOH/g, respectively. Therefore, AV of OF's obtained with sulfided CoMo/γ-Al_2O_3 was 1.6 mg KOH/g lower than for reduced CoMo/γ-Al_2O_3catalyst.

For the OF of PTBO with reduced CoMo/γ-Al_2O_3 and sulfided CoMo/γ-Al_2O_3 the HHV was more than double with an increase from 19.0 MJ/Kg to 44.4 and 44.2 MJ/Kg respectively. After hydroprocessing the OF HHV with reduced CoMo/γ-Al_2O_3 and sulfided CoMo/γ-Al_2O_3 catalysts increased from 19.0 MJ/Kg to 43.1 and 44.4 MJ/Kg respectively. The respective percent WC values of the OF with reduced CoMo/γ-Al_2O_3 and sulfided CoMo/γ-Al_2O_3 catalysts were reduced to 0.2 and 0.1% of the value of 21.0 for PTBO.

Table 5.2 Comparison of properties of AV, HHV, percent WC, CHNO

Properties	Control (PTBO)	Reduced(2014)/ CoMo/γ-Al_2O_3	Sulfided CoMo/γ-Al_2O_3
AV (mg KOH/g)	223.0	2.1	0.5
HHV, MJ/Kg	19.0	43.1	44.4
Water content (%)	21.0	0.2	0.1
Elemental analysis (%)			
C	43.1	86.3	86.7
H	8.9	13.4	13
N	0.2	0.4	0.4
O	47.8	0.1	0
HCF Yield (g/g of feed, based on dry weight of biomass)	NA	0.02	0.23

(2014)\ Adapted from Parapati et al. 2014.
(O obtained by substraction) and yields between PTBO control, and OF's obtained with reduced CoMo/γ-Al_2O_3 and sulfided CoMo/γ-Al_2O_3 catalysts.

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The CHNO properties produced by the two catalysts differed little. The OF yield was 0.23 g/g of feed, which was higher for the treatment with sulfided CoMo/γ-Al_2O_3, compared to 0.02 g/g of feed OF yields for the reduced CoMo/γ-Al_2O_3 catalyst. These results show that the treatment with sulfided CoMo/γ-Al_2O_3 provided the best results in terms of OF yields as well as quality (HHV, AV, and WC).

Table 5.3 shows gas analysis results of non-condensable gas samples collected during hydroprocessing experiments for reduced CoMo/γ-Al_2O_3 and sulfided CoMo/γ-Al_2O_3 catalysts. From Table 5.3, it is evident that hydroprocessing with the sulfided CoMo catalyst resulted in higher hydrogen consumption compared to hydroprocessing with the reduced CoMo/γ-Al_2O_3 catalyst. This high hydrogen consumption indicates higher deoxygenation for sulfided CoMo/γ-Al_2O_3. This provides an explanation for the relatively better physical and chemical properties of OF obtained with sulfided CoMo/γ-Al_2O_3 treatment.

Table 5.3 Gas analysis of reduced CoMo/γ-Al_2O_3 and sulfided CoMo/γ-Al_2O_3 catalysts.

Catalyst	H_2 %	O_2 %	N_2 %	CH_4 %	CO %	CO_2 %	C_2H_6 %
Reduced CoMo/γ-Al_2O_3	69.8	0.3	0.7	5.7	0.2	1.7	0.9
Sulfided CoMo/γ-Al_2O_3	64.4	1.2	3.8	1.5	0.05	2.7	1.1

5.5.1.1 DHA analysis

Figure 5.3 shows the DHA of mixed liquid hydrocarbons obtained with reduced CoMo/γ-Al_2O_3 and sulfided CoMo/γ-Al_2O_3 catalyst, performed according to ASTM D6730-01. For the reduced CoMo/γ-Al_2O_3 catalyst, the olefins, iso-paraffins, naphthenes

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and compounds greater than C14 dominated the mixed liquid hydrocarbons followed by aromatics and paraffins with an octane value of 52.3 (Parapati et al., 2014). In comparison, the DHA of the sulfided CoMo/γ-Al_2O_3 catalyst upgraded product mainly contained iso-paraffins, olefins, naphthenes and paraffins over compounds greater than C14 and aromatics with an octane value of 68.4.

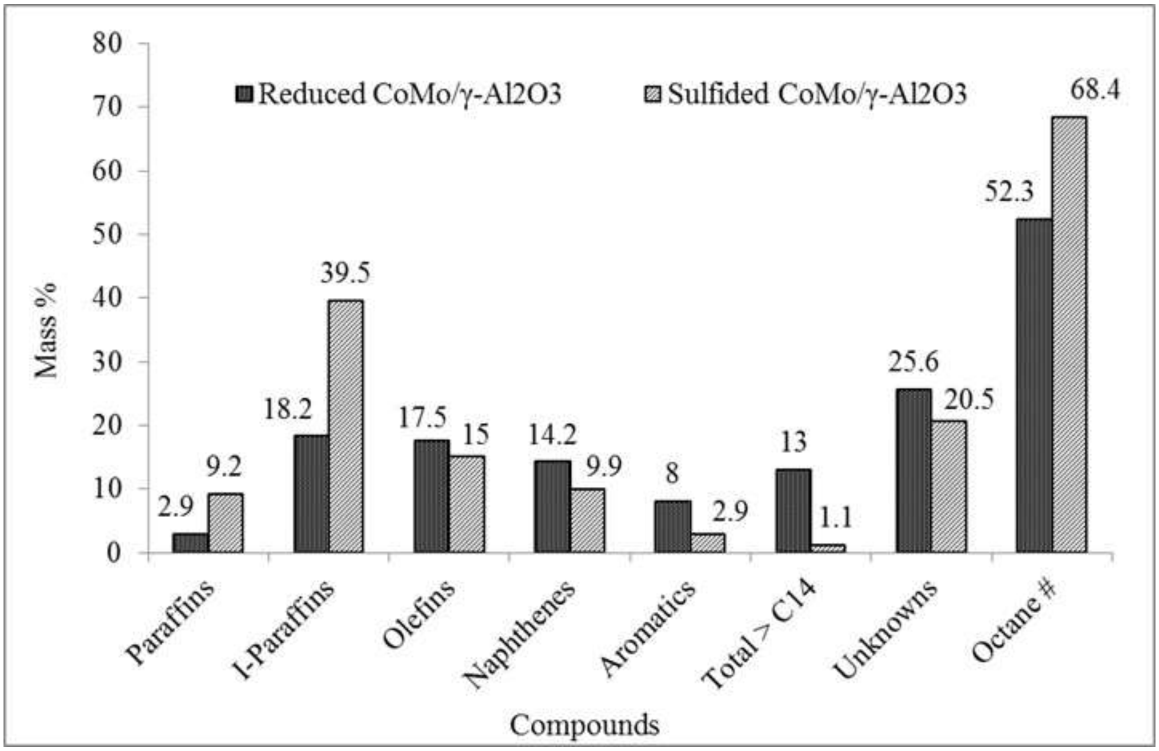

Figure 5.3 DHA of mass percentage (%) of OF's obtained from reduced CoMo/γ-Al_2O_3 and sulfided CoMo/γ-Al_2O_3 treatments.

5.5.1.2 SIMDIS analysis

Figures 5.4 and 5.5 compare the SIMDIS results (by ASTM D2887) of the reduced CoMo/γ-Al_2O_3 and sulfided CoMo/γ-Al_2O_3 OF. SIMDIS of the reduced

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$CoMo/\gamma\text{-}Al_2O_3$ OF showed the Initial Boiling Point (IBP) and Final Boiling Point (FBP) to be 69 °C and 304 °C, respectively.

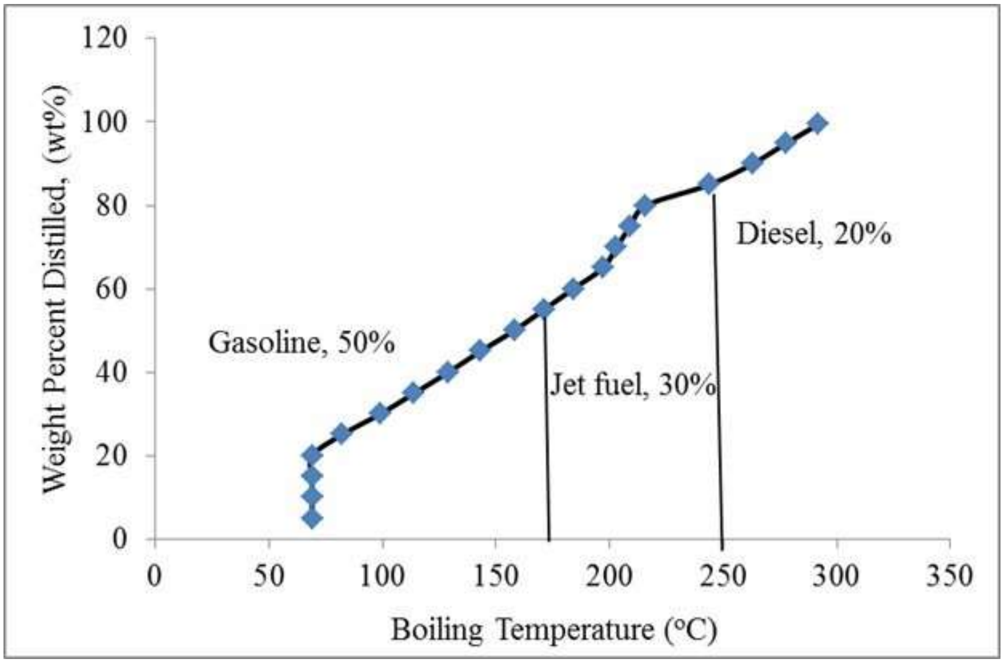

Figure 5.4 Weight percent (wt%) distilled vs boiling temperature (°C) of the reduced $CoMo/\gamma\text{-}Al_2O_3$ upgraded liquid fuel determined by SIMDIS.

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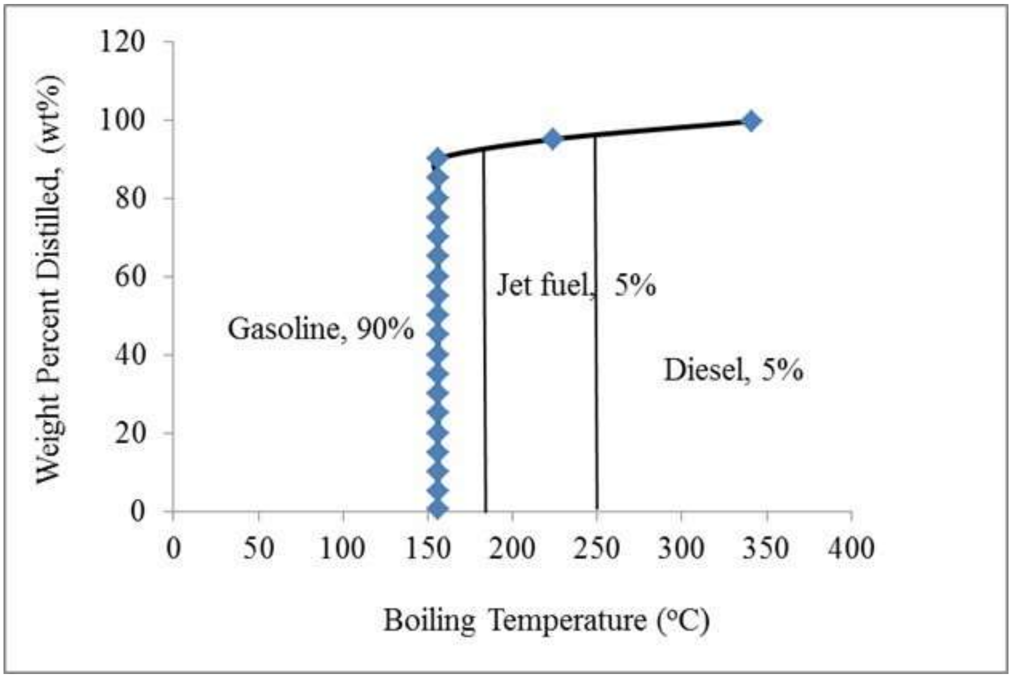

Figure 5.5 Wt% distilled vs boiling temperature (°C) of the sulfided CoMo/γ-Al_2O_3 upgraded liquid fuel determined by SIMDIS.

From the SIMDIS results, it was reported that the OF produced by reduced CoMo/γ-Al_2O_3 had a boiling temperature range of 69 to 304 °C, and contained petroleum equivalents of 50% gasoline (38 -170 °C), 30% jet fuel (170-250 °C) and 20% diesel (250-304 °C) range hydrocarbons (Parapati et al., 2014). By comparison to the SIMDIS results for the reduced CoMo/γ-Al_2O_3

OF, the sulfided CoMo/γ-Al_2O_3 OF showed IBP and FBP to be 156 °C and 341 °C, respectively. The sulfided CoMo/γ-Al_2O_3 OF contained petroleum equivalents of 90% gasoline (156 °C), 5% jet fuel (156-224 °C) and 5% diesel (224-341 °C) range hydrocarbons.

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5.5.1.3 Thermogravimetric Analysis (TGA)

TGA was performed on the used catalysts to determine the amount of residual carbon deposited on the catalyst surface. A Shimadzu instrument TGA-50 was used to perform the TG analysis. A required amount of catalyst was placed in an alumina pan and a temperature program was ramped up at a rate of 5 °C/min starting at room temperature and terminating at 800 °C. The runs were performed under air flow of 50 mL/min. The percentage weight loss of the fresh CoMo/γ-Al_2O_3, fresh sulfided CoMo/γ-Al_2O_3, spent reduced CoMo/γ-Al_2O_3 catalyst, spent sulfided CoMo/γ-Al_2O_3 catalyst from the hydroprocessing of pretreated bio-oil and raw bio-oil are shown in Figures 5.6, 5.7, 5.8 and 5.9.

Figures 5.6, 5.7, 5.8 and 5.9 show significant loss during the intial heating period at the temperature range between 100 to 220 ºC. This weight loss was due to the removal of moisture from the catalyst surface and also moisture from the interior of the pores. Part of the weight loss could also be due to the removal of easily oxidizable carbonaceous species formed during initial decomposition of the aromatic compounds. Further the water which was bound with the catalyst material requires higher temperature for desorption. In the case of TGA analysis of fresh CoMo/γ-Al_2O_3 (Figure 5.6) and fresh sulfided CoMo/γ-Al_2O_3 (Figure 5.7) no weight loss was observed due to carbon deposition. However, in the case of of spent reduced CoMo/γ-Al_2O_3 (Figure 5.8), catalyst weight loss of 0.6 mg was observed at a temperature between 443 to 521 °C, which indicates that there was more carbon deposition on the surface of the spent reduced catalyst in comparison to spent sulfided CoMo/γ-Al_2O_3 (Figure 5.9) from PTBO treatment, which had catalyst weight loss of only 0.3 mg at a temperature between 391 to

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519 °C. In either the cases almost negligible or very little carbon deposition was observed.

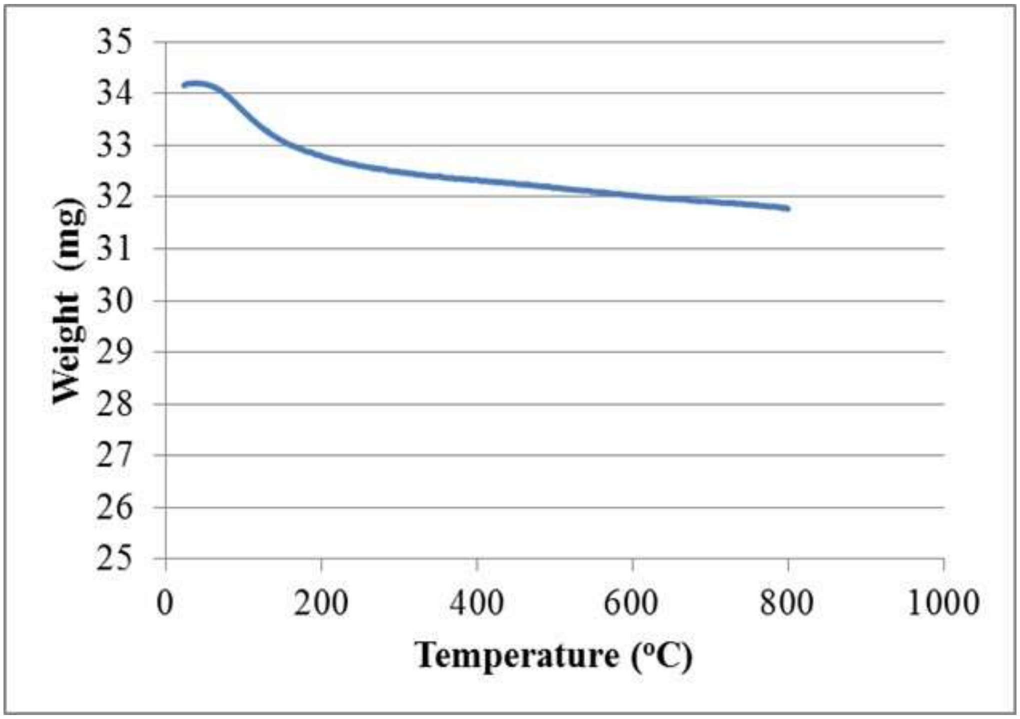

Figure 5.6 TGA of the fresh CoMo/γ-Al_2O_3 catalyst.

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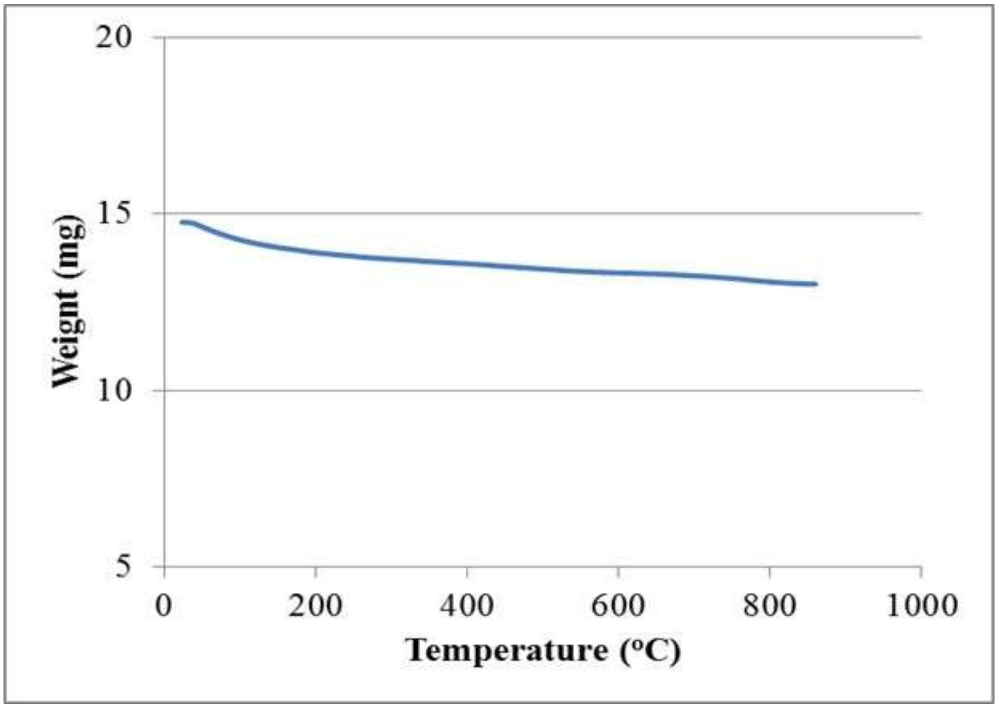

Figure 5.7 TGA of the fresh sulfided CoMo/γ-Al_2O_3 catalyst.

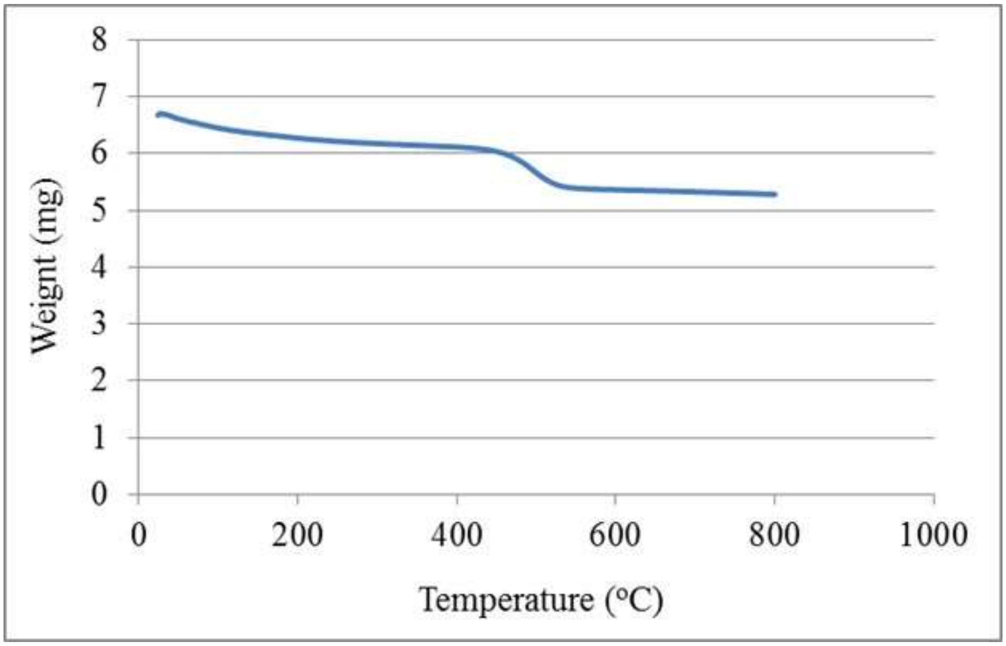

Figure 5.8 TGA of the used reduced CoMo/γ-Al_2O_3 catalyst from the hydroprocessing of PTBO.

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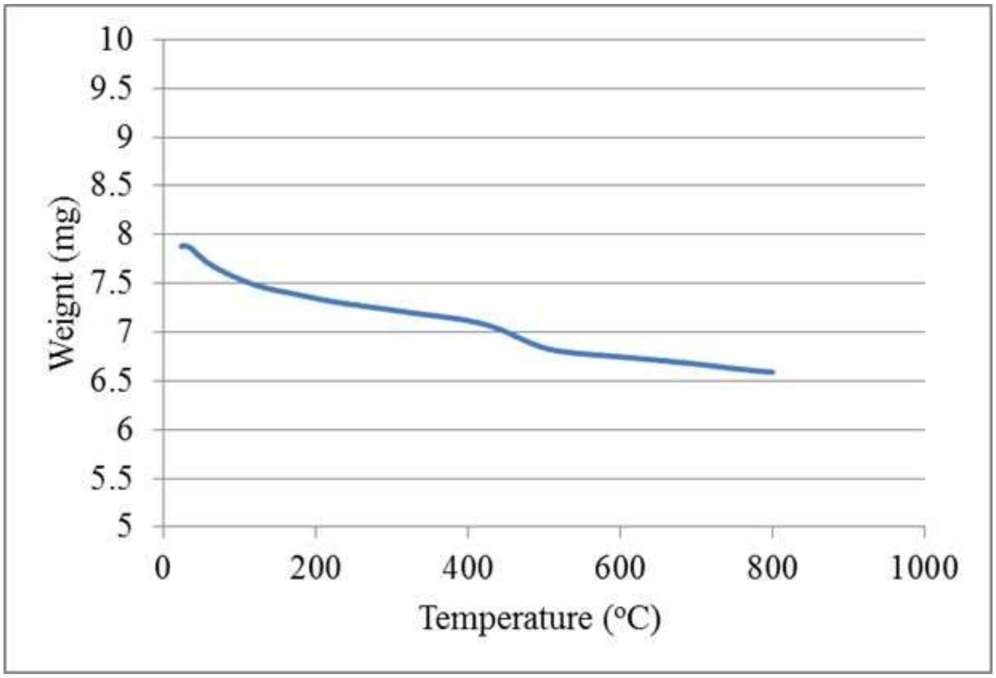

Figure 5.9 TGA of the used sulfided CoMo/γ-Al_2O_3 catalyst from the hydroprocessing of PTBO.

5.5.2 Comparison of hydroprocessed product obtained from RBO and PTBO

The experimental methods and materials were decribed in section 5.3 and will not be repeated here. Table 5.5 shows the properties of OF obtained by the hydroprocessing of the RBO and PTBO. The properties of the RBO and PTBO control are shown in Table 4.5 to allow comparison with the properties of OF's obtained on hydroprocessing RBO and PTBO with sulfided CoMo/γ-Al_2O_3 catalysts. The experiments with best results were performed for 3 times. Table 5.5 indicates that after hydroprocessing of RBO and PTBO with the sulfided CoMo/γ-Al_2O_3 catalyst, the AV decreased from 96.5 of RBO 0 to 0.8 and 241.0 of PTBO to 0.5 mg KOH/g, respectively. Therefore, AV of OF's obtained with sulfided CoMo/γ-Al_2O_3 for PTBO was 0.3 mg KOH/g lower than for OF of RBO 0.

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For the OF of RBO and PTBO with the sulfided CoMo/γ-Al_2O_3 catalyst, the HHV was more than double with an increase from 16.5 to 43.4 MJ/Kg for RBO and from 19.0 to 44.4 for PTBO. The respective percent WC values of the OF with sulfided CoMo/γ-Al_2O_3 catalysts for RBO and PTBO were reduced to 0.8 and 0.1% of the value of 28.9 for RBO and 21.0 for PTBO.

Table 5.4 Comparison of properties of AV, HHV, percent WC, CHNO

Properties	Control (RBO)	OF of RBO	Control (PTBO)	OF of PTBO
AV (mg KOH/g)	96.5	0.8	223	0.5
HHV, MJ/Kg	16.5	43.4	19	44.4
Water content (%)	28.9	0.8	21	0.1
Elemental analysis (%)				
C	37.6	86.1	43.1	86.7
H	7.7	13	8.9	13
N	0.1	0.5	0.2	0.4
O	54.7	0.5	47.8	0
S	0.0	0.0	0.46	0.0
HCF Yield (g/g of feed, based on dry weight of biomass)	NA	0.2	NA	0.23

(O obtained by substraction) and yields between RBO and PTBO control, and OF's obtained on hydroprocessing RBO and PTBO with sulfided CoMo/γ-Al_2O_3 catalyst.

The CHN properties produced by the two OF's (RBO and PTBO) differed little. The elemental oxygen was 0.5% lower for OF of PTBO than elemental oxygen of RBO. The OF yield was 0.23 g/g of feed for the treatment with PTBO, and 0.2 g/g of feed for the treatment with RBO; both differed only by 0.03%. These results show that the treatment with PTBO provided the best results in terms of properties (HHV, AV, elemental oxygen percentage and WC) in comparison to RBO.

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5.5.2.1 Gas analysis

Table 5.5 shows gas analysis results of non-condensable gas samples collected during hydroprocessing experiments for RBO and PTBO. From Table 5.5, it is evident that hydroprocessing with the PTBO resulted in higher hydrogen consumption compared to hydroprocessing with the RBO. This high hydrogen consumption indicates higher deoxygenation for PTBO.

Table 5.5 Gas analysis of RBO and PTBO treatments.

Catalyst	H_2 %	O_2 %	N_2 %	CH_4 %	CO %	CO_2 %	C_2H_6 %
RBO treatment	67.8	0.5	1.8	2.9	0.08	5.04	2.86
Sulfided CoMo/γ-Al_2O_3	64.4	1.2	3.8	1.5	0.05	2.7	1.1

5.5.2.2 DHA analysis

Figure 5.10 shows the DHA of mixed liquid hydrocarbons obtained with RBO treatment and PTBO treatment, perfomed according to ASTM D6730-01. For the RBO treatment, the naphthenes, olefins, iso-paraffins, naphthenes and compounds greater than C14 dominated the mixed liquid hydrocarbons followed by aromatics and paraffins with an octane value of 56.2. In comparison, the DHA of the sulfided CoMo/γ-Al_2O_3 catalyst upgraded product mainly contained iso-paraffins, olefins, naphthenes and paraffins over compounds greater than C14 and aromatics with an octane value of 68.4.

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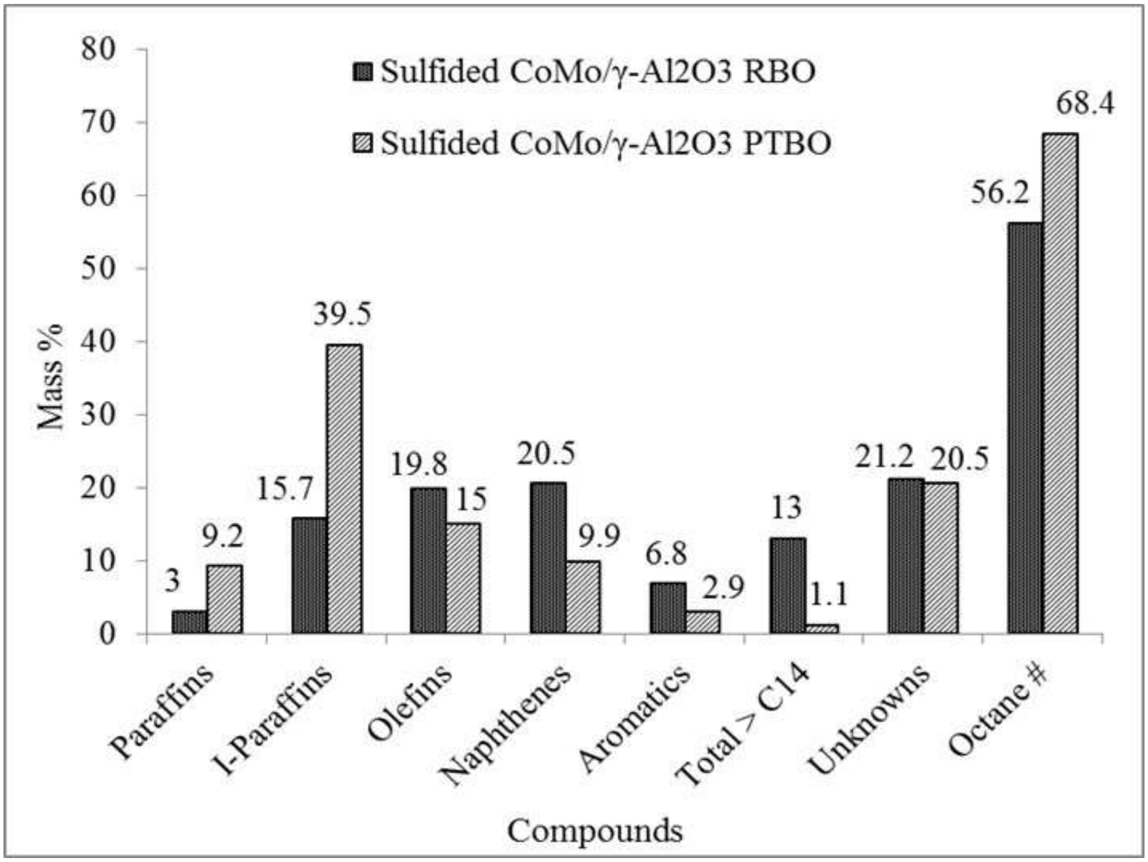

Figure 5.10 DHA of mass percentage (%) of OF's obtained from RBO and PTBO treatments.

5.5.2.3 Thermogravimetric Analysis (TGA)

TGA was performed on the used catalysts to determine the amount of residual carbon deposited on the catalyst surface. A Shimadzu instrument TGA-50 was used to perform the TG analysis. A required amount of catalyst was placed in an alumina pan and a temperature program was ramped up at a rate of 5 °C/min starting at room temperature and terminating at 800 °C. The runs were performed under air flow of 50 mL/min. The percentage weight loss of the fresh CoMo/γ-Al_2O_3, fresh sulfided CoMo/γ-Al_2O_3, spent

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reduced CoMo/γ-Al_2O_3 catalyst, spent sulfided CoMo/γ-Al_2O_3 catalyst from the hydroprocessing of RBO and PTBO are shown in Figures 5.11, 5.12, 5.13 and 5.14.

Figures 5.11, 5.12, 5.13 and 5.14 show significant loss during the intial heating period at the temperature range between 100 to 220 ^{o}C. This weight loss was due to the removal of moisture from the catalyst surface and also moisture from the interior of the pores. Part of the weight loss could also be due to the removal of easily oxidizable carbonaceous species formed during initial decomposition of the aromatic compounds. Further the water which was bound with the catalyst material requires higher temperature for desorption. In the case of TGA analysis of fresh CoMo/γ-Al_2O_3 (Figure 5.11) and fresh sulfided CoMo/γ-Al_2O_3 (Figure 5.12) no weight loss was observed due to carbon deposition. However in the case of of spent CoMo/γ-Al_2O_3 (Figure 5.13) from RBO treatment, catalyst weight loss of 6.5 mg was observed at a temperature between 267 to 529 °C, which indicates that there was more carbon deposition on the surface of the catalyst. By contrast, spent CoMo/γ-Al_2O_3 (Figure 5.14) from PTBO 2 treatment, catalyst weight loss of 0.3 mg of weight loss was observed at a temperature between 391 to 519 °C, which indicates that there was negligible or very little carbon deposition on the surface of the spent catalyst from PTBO treatment in comparison to carbon deposition (6.5 mg) on catalyst surface from RBO treatment.

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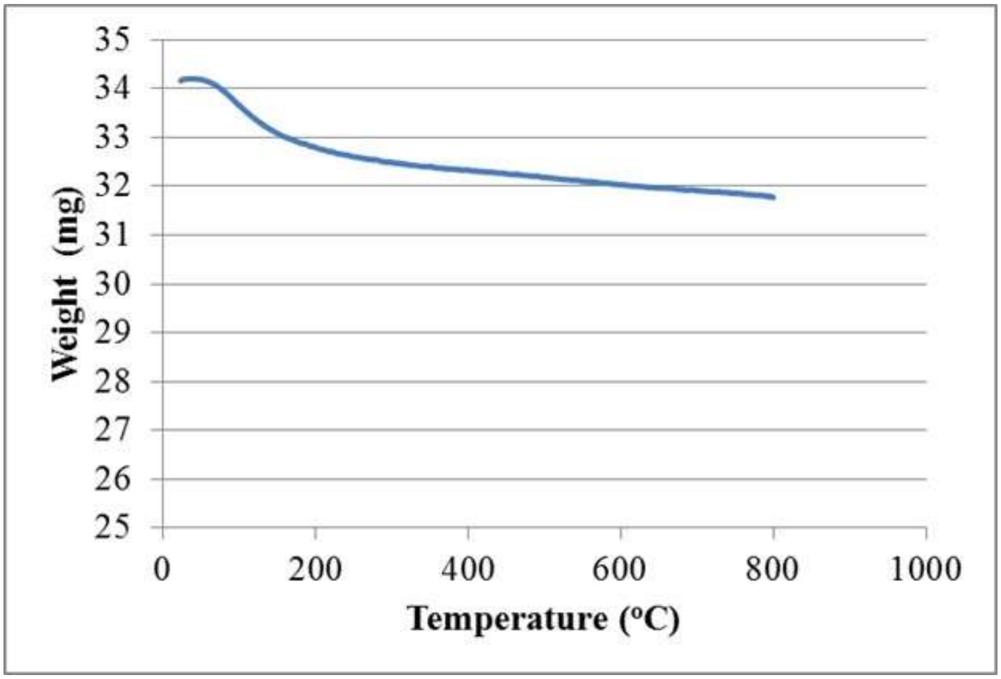

Figure 5.11 TGA of the fresh CoMo/γ-Al_2O_3 catalyst.

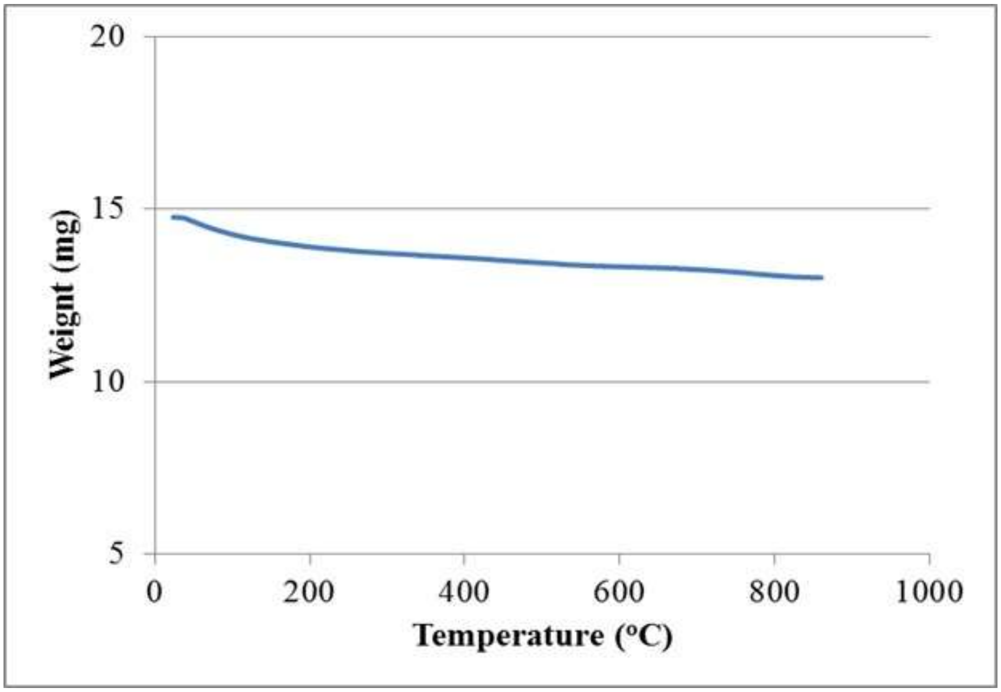

Figure 5.12 TGA of the sulfided CoMo/γ-Al_2O_3 catalyst.

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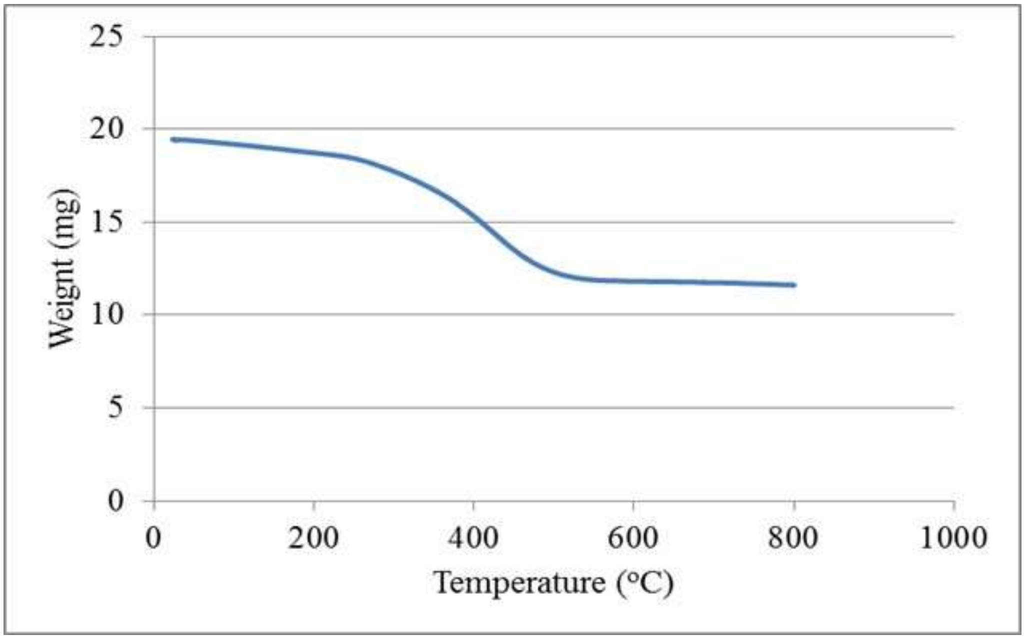

Figure 5.13 TGA of the used sulfided CoMo/γ-Al_2O_3 catalyst from the hydroprocessing of RBO.

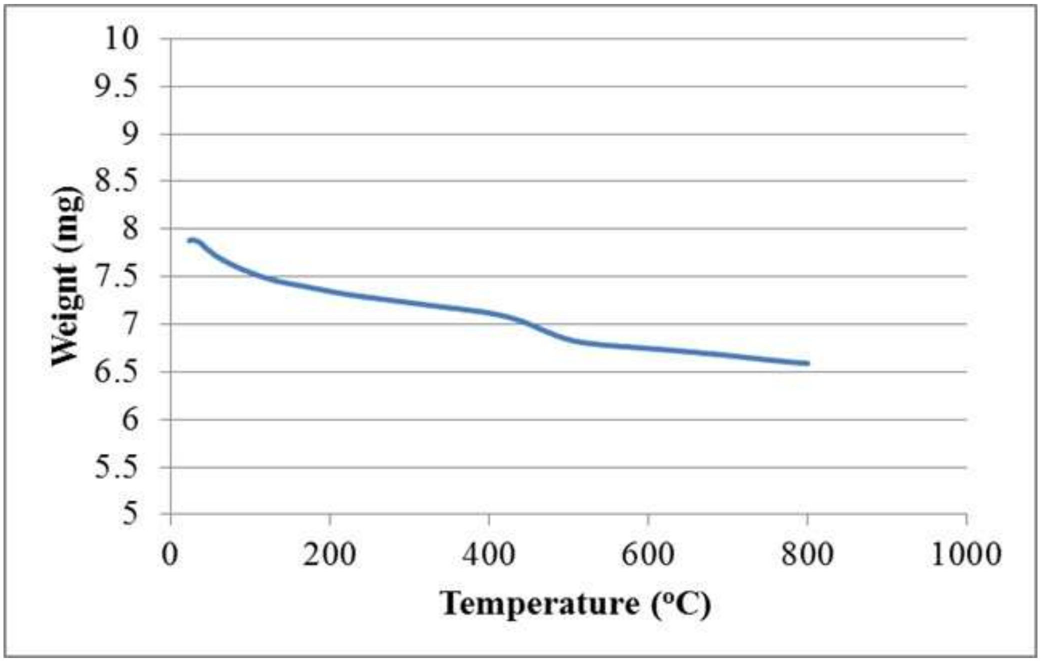

Figure 5.14 TGA of the used sulfided CoMo/γ-Al_2O_3 catalyst from the hydroprocessing of PTBO.

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5.5.2.4 Trace metal analysis

Trace metal analysis of control RBO 0 and control PTBO 2, OF of RBO 0 and OF of PTBO 2 was performed on a PerkinElmer SCIEX ICP Mass Spectrometer (ELAN DRC II) (using nebulizer gas flow of 0.85 L/min, ICP RF power of 1100 watts, lens voltage of 7.8 volts, analog stage volts of 1800 watts, pluse stage volts of 900 volts, average vacuum pressure of 6 x 10^{-6} torr). These analysis results were provided by the Chemistry Department, Mississippi State University.

Table 5.6 shows trace metal analysis of control samples of RBO and PTBO. Control RBO (feedstock/untreated) contained elements of Cu, Ti, Si, Mo, Al, Mg, Mn and Zn.

Table 5.7 shows the trace metal analysis of OF of RBO and PTBO. OF of PTBO contained less amounts of Cu, Si, Al, and Zn in comparison to OF of RBO. Treated PTBO and RBO contained less amounts of Cu, Ti, Si, Mo, Al, Mg, Mn and Zn in comparison to control samples (RBO and PTBO).

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Table 5.6 Trace metal analysis of control RBO and PTBO.

Element/Isotope	**Control RBO**	**Control PTBO**
	Conc. (ug/L)	**Conc. (ug/L)**
Cu-63	57.4	101
Ti-47	0.0102	0.0253
Si-28	0.726	0.726
Mo-98	0.017	0.221
Al-27	73.3	0.595
Mg-24	0.0536	0.0536
Cu-65	57.6	101
Ti-46	0.0736	0.0869
Ti-48	0.165	0.22
Ti-49	0.00527	0.0648
Ti-50	0.0624	1.73
Si-29	0.0259	0.0259
Si-30	0.0277	0.0277
Mo-92	0.0256	0.218
Mo-94	0.0298	0.22
Mo-95	0.0173	0.222
Mo-96	0.0183	0.219
Mo-97	0.017	0.221
Mg-25	0.228	23.1
Mg-26	0.332	0.332
Mn-55	58.9	89.5
Zn-66	126	284
Zn-64	139	320
Zn-67	142	321
Zn-68	144	321
Zn-70	157	283

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Table 5.7 Trace metal analysis of OF of RBO and PTBO.

Element/Isotope	OF of RBO	OF of PTBO
	Conc. (ug/L)	Conc. (ug/L)
Cu-63	34.7	31.7
Ti-47	0.00504	0.0052
Si-28	64.7	60.5
Mo-98	0.000387	0.00161
Al-27	43.9	39.1
Mg-24	0.176	0.183
Cu-65	35	31.6
Ti-46	0.0436	0.0415
Ti-48	0.00949	0.0147
Ti-49	0.00336	0.00393
Ti-50	0.00732	0.0101
Si-29	0.282	0.232
Si-30	0.0277	0.0277
Mo-92	0.000506	0.00184
Mo-94	0.000605	0.00193
Mo-95	0.000419	0.00164
Mo-96	0.00043	0.00165
Mo-97	0.000386	0.00162
Mg-25	0.102	0.105
Mg-26	0.18	0.184
Mn-55	0.448	0.438
Zn-66	9.93	9.37
Zn-64	11	10.3
Zn-67	11.3	10.8
Zn-68	11.4	10.9
Zn-70	11.6	11.8

5.6 Conclusion

This study extended the results of a previous screening of four catalysts applied to perform single-stage hydroprocessing to PTBO. The PTBO was produced by oxidation

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with 3 wt% ozone and 10 wt% hydrogen peroxide followed by the addition of 25 wt% butyric anhydride. The previous study results showed that in comparison with 3 other catalysts, reduced CoMo/γ-Al_2O_3 catalyst produced the best results for single-stage hydroprocessing of PTBO. While the physical and chemical properties of the hydroprocessed PTBO catalyzed by reduced CoMo/γ-Al_2O_3 were satisfactory, the yield was low. The current study tested the hypothesis that sulfided CoMo/γ-Al_2O_3 would outperform reduced CoMo/γ-Al_2O_3 when applied to single-stage hydroprocessing. This method provided a HCF with a HHV of 44.4 MJ/kg, AV of 0.5 mg KOH/g, percent WC of 0.1% and percent O value of negligible amount(~0). The HCF or OF obtained with sulfided CoMo/γ-Al_2O_3 contained petroleum equivalents of 90% gasoline, 5% jet fuel and 5% diesel range hydrocarbons and OF yields were increased to 0.23 g/g of feed to 0.02 g/g of feed in comparison to reduced CoMo/γ-Al_2O_3 catalyst. From TGA analysis coke deposition was less or negligible on sulfided CoMo/γ-Al_2O_3 catalyst. Therefore, sulfided CoMo/γ-Al_2O_3 catalyst showed much better performance than reduced CoMo/γ-Al_2O_3 catalyst in a single-stage hydroprocessing of PTBO.

The current study tested the hydroprocessing of RBO and PTBO with sulfided CoMo/γ-Al_2O_3 by single-stage hydroprocessing. In comparison to OF of RBO, OF of PTBO showed 0.5% lower oxygen content, 0.3 mg KOH/g AV, 1.0 MJ/kg higher HHV and 0.7% lower AV. The yields obtained with treated PTBO were 0.03 wt% more than treated RBO. From DHA analysis, for the RBO treatment, the naphthenes, olefins, iso-paraffins, naphthenes and compounds greater than C14 dominated the mixed liquid hydrocarbons followed by aromatics and paraffins with an octane value of 56.2. In comparison, the DHA of the sulfided CoMo/γ-Al_2O_3 catalyst upgraded product mainly

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contained iso-paraffins, olefins, naphthenes and paraffins over compounds greater than C14 and aromatics with an octane value of 68.4.

Therefore, sulfided CoMo/γ-Al_2O_3 catalyst with PTBO hydroprocessing showed much better performance than sulfided CoMo/γ-Al_2O_3 catalyst with RBO hydroprocessing in a single-stage hydroprocessing of PTBO. TGA analysis showed more catalyst weight loss (6.5 mg) with RBO treatment than PTBO treatment (0.3 mg). In addition OF of PTBO contained less amounts of Cu, Ti, Si, Mo, Al, Mg, Mn and Zn elements than OF of RBO. PTBO performance was superior in comparision to RBO, this was due to less amounts of aldehydes and ketones presence in the PTBO control than RBO control sample.

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CHAPTER VI

DEACTIVATION AND REGENERATION STUDIES

6.1 Abstract

Catalyst deactivation and regeneration studies were performed for three feedstocks, raw bio-oil, pretreated bio-oil with and without added butyric anhydride. The objective was to determine the life of the the sulfided CoMo/γ-Al_2O_3 catalyst activity at a previously determined most effective temperatures, hydrogen pressures, liquid hourly space velocity and hydrogen flow rate (375-400 °C, 1500 psig, 0.3 h^{-1}, 1000 ml/min). The longest run time of 19.2 h was observed for pretreated bio-oil with butyric anhydride addition. For this longest run time for pretreated bio-oil with butyric anhydride the acid value, heating value, oxygen content and water content properties were the lowest as observed. After two catalyst regenerations of the sulfided CoMo/γ-Al_2O_3 catalyst, the best properties, run times and yields were obtained for pretreated bio-oil with butyric anhydride addition in comparison to raw bio-oil and pretreated bio-oil without butyric anhydride. The product organic fraction was analyzed by GC-MS and elemental analysis. Scanning electron microscopic analysis was performed on the catalyst (fresh, sulfided, initial run, first and second regenerated spent catalysts) of best performing feedstock pretreated bio-oil with butyric anhydride addition.

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6.2 Introduction

Bio-oil upgrading is required for its utilization in most applications. Currently tested upgrading techniques include hydrodeoxygenation (HDO) (Pindoria et al., 1997, Pindoria et al., 1998, Zhang et al., 2003, Sandra et al., 1994, Senol et al., 2005), catalytic cracking of pyrolysis vapours (Nokkosmaki et al., 2000), steam reforming (Wang wt al., 1997, Wang et al., 1998), emulsification (Chiaramonti et al., 2003), chemical extraction, esterification (Zhang et al., 2006, Xu et al., 2006) and olefination (Zhang et al., 2011, Zhang et al., 2013, Chatterjee et al., 2013). Other studies that involve removal of oxygen in the form of CO or CO_2 are by decarbonylation and decarboxylation reactions by thermal or catalytic processes (Mercarder et al., 2010). Many practitioners have applied HDO to bio-oil to produce liquid hydrocarbons.

Elliott et al. (2012) reported on two-stage catalytic hydroprocessing of pine fast pyrolysis oil in a bench scale continuous-flow fixed-bed catalytic reactor system to evaluate the performance of fully sulfided catalyst beds including both ruthenium and promoted molybdenum. A two-stage treatment was employed at a temperature of approximately 170 ^oC and at an LHSV of 0.19 with sulfided Ru/C catalyst. This was followed by a second stage hydrocracking treatment at a temperature of 400 ^oC for the same LHSV with both sulfided CoMo and NiMo. The HDO was operated for 90 to 99 h depending on the catalyst type. The hydroprocessed product had densities of 0.82 to 0.92 g/ml, oxygen content ranging from 0.2 to 2.7 wt %, and total acid number ranging from 0.01 to 2.7 mg KOH/g.

Wang et al. (2014) hydrotreated diluted liquefied bio-oil (1:9 ratio of bio-oil and 1-methylnaphthalene) in a fixed bed microreactor over sulfided $NiMo/Al_2O_3$ catalyst at a

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temperature ranging from 280 to 350 °C, pressures ranging from 500 to 1400 psi, hydrogen flow rate of 100 ml/min, and LHSV ranging from 0.4 to 2.0 h^{-1}. The upgraded bio-oil acid value decreased from 23.0 mg KOH/g (raw bio-oil) to 2-8 mg KOH/g. Researchers concluded that high hydrogen pressures, high temperature and low LHSV favor the production of high quality bio-oils with low acid value. Researchers also investigated the deactivation of $NiMo/Al_2O_3$; the catalyst was deactivated after 240 h of operation.

An unsolved problem encountered in HDO of bio-oil is catalyst deactivation. Catalyst deactivation occurs due to poisoning by nitrogen species or water, sintering of the catalyst, metal deposition (mainly due to alkali metals) or coking (Wildschut et al., 2009). The extent of coking depends on the catalyst type and reaction conditions. Carbon deposition on the catalyst surface has proven to be the main problem for catalyst deactivation (Furimsky and Massoth 1999). The carbon deposition is mainly due to polycondensation and polymerization reactions on the surface of the catalyst, forming polyaromatic species, which lead to blockage of active sites on the catalyst (Furimsky and Massoth 1999).

Furimsky and Massoth (1999) observed that the rates of the carbon forming reactions were controlled by the rate of bio-oil fed to the system. In addition, process conditions played an important role. For oxygen containing hydrocarbons, compounds containing more than one oxygen atoms, it was observed that these compounds have higher affinity for carbon formation on the surface of the catalysts by polymerization reactions (Furimsky and Massoth 1999). Coking was noted to have increased with

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increase in catalyst acidity, as influenced by both Lewis and Bronsted acid sites. To minimize coke formation proper choice of process parameters is important.

Xu et al. (2011) performed oxidation of raw bio-oil via ozone pretreatment to convert aldehydes to acids. Parapati et al. (2014) and Steele et al. (2013) have described the production of pretreated bio-oil. Parapati et al. (2014) tested one embodiment of the Steele et al. patent by oxidizing raw bio-oil with 3 wt% oxone combined with 10 wt% hydrogen peroxide with a final addition of 25 wt% of butyric anhydride. Parapati et al. (2014) performed hydroprocessing of pretreated bio-oil with butyric anhydride addition using four different catalysts with pressurized hydrogen gas (1500 psig) and determined that reduced CoMo/γ-Al_2O_3 produced the best hydrocarbon properties. However, the reduced CoMo/γ-Al_2O_3 yield was low at only 0.02 g/g of feed (based on dry biomass weight). Parapati et al. (2014, In review) also further employed a sulfided CoMo/γ-Al_2O_3 catalyst to improve the oganic fraction (OF) yields. It is well know that buyric anhydride reacts with water to form acids and reacts with alcohols to form corresponding esters.

The objective of this research was to focus on catalyst deactivation and regeneration studies to determine the catalytic activity of sulfided CoMo/γ-Al_2O_3 catalyst and also to determine the performance among the three tested feedstocks (raw bio-oil, pretreated bio-oil with and with out butyric anhydride addition) at a temperature of 375-400 °C, hydrogen pressure of 1500 psig, liquid hourly space velocity (LHSV) of 0.3 h^{-1}, and hydrogen flow rate of (HFR) 1000 ml/min experimental process conditions.

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6.3 Experimental

6.3.1 Materials

Oxone, hydrogen peroxide (H_2O_2) 30 wt% solution in water and butyric anhydride were purchased commercially from Sigma-Aldrich. CoMo/γ-Al_2O_3 (3.4-4.5% Co and 11.5-14.5% Mo on gamma-alumina support) were purchased from Alfa Aesar. Cyclohexane and carbondisulfide were purchased from Fisher Scientific. The oxide form of catalysts was activated by subjecting them to a sulfidation process prior to hydroprocessing experiments. CoMo/γ-Al_2O_3 was sulfided with a solvent mixture of 2 vol % carbon disulfide and cyclohexane. To 800 ml of cyclohexane solvent, 16 ml (2 vol %) of carbon disulfide was added and the solvent mixture was pumped through a high-pressure dual-pump system. Sulfiding of the catalyst was performed at 300 ^{o}C, a pressure of 750 psi and LHSV of 1 h^{-1} for a period of 4 hrs. The catalyst was regenerated at a temperature range of 400 to 600 ^{o}C for 4 h followed by resulfidation as described above. Raw bio-oil (RBO 0) was produced by fast pyrolysis process at a temperature of 400-450 ^{o}C under nitrogen gas atmosphere using a 7 kg/h auger-fed pyrolysis reactor located in the Department of Sustainable Bioproducts, Mississippi State University.

6.3.2 Methods

6.3.2.1 Pretreatment of bio-oil

The pretreatment of raw bio-oil (PTBO 1) was performed at ambient temperature and pressure in a Parr autoclave (450 ml) equipped with an electronic stirrer. Bio-oil oxidation was performed by the addition of 3 wt% oxone and 10 wt% H_2O_2 and the mixture was stirred for 90 min at room temperature.

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The pretreatment of raw bio-oil (PTBO 2) was performed as described above except that after 90 min of stirring at ambient temperature and pressure in a Parr autoclave (450 ml) 25 wt% butyric anhydride was added. The pretreated bio-oil with added butyric anhydride was then stirred for 90 min at 90 °C to obtain the final experimental PTBO 2.

6.3.2.2 Continuous packed-bed reactor

The continuous packed-bed reactor (Figure 6.1) used in the experimentsconsisted of a 1” I.D tubular reactor enclosed in a three-zone furnace (three 6” zones each independently controlled by its own temperature controller) followed by a condensation system. The temperatures inside the reactor were monitored with a point profile thermocouple equipped with ten sensing points (Omega Instruments). Three temperature sensing points were located in each of the 3 reactor heater zones for a total of 9. The tenth temperature sensing point was located at the condenser orifice. The catalyst bed temperature zones were maintained as closely as possible to the desired temperature set point through the course of the experiment. The catalytic reaction is exothermic such that temperatures are difficult to control due to the adiabatic nature of the reaction. Temperature control was only possible within a temperature range (for example 375-400 °C). The bio-oil was pumped into the catalyst tube with a high pressure dual-pump system (Teledyne Isco 500D). The hydrogen flow rate was controlled with a mass flow controller (MFC; Brooks Instruments), and the reactor pressure was controlled with a back-pressure regulator. A schematic diagram of the reactor is shown in Figure 6.1.

For all experiments the reactor was loaded with catalyst at a temperature initially set to 150 °C. Figure 6.1 shows a diagram of the schematic of the continuous packed-bed

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reactor. Figure 6.2a and 6.2b shows the method of catalyst loading in the continuous packed-bed reactor. For all experiments reactor was loaded with catalyst at a temperature initially set to 150 °C. Once this initial temperature set point was attained, the reactor temperature was raised by another 100 °C upon reading the resultant temperature of 250 ºC and the reactor temperature was again raised to 350 °C. A final 25 to 50 ºC increase was often applied to raise the actual reaction temperature as close to 375 ºC as possible (for example 375-400 ºC). The reactor was pressurized to the desired 1500 psi hydrogen reaction pressure. Hydroprocessing of raw bio-oil was performed in a continuous packed-bed reactor utilizing sulfided CoMo/γ-Al_2O_3 catalyst. Process conditions were varied to determine the most effective temperature (325-350, 375-400, 400-425°C), pressure (1000, 1500 psig), hydrogen flow rate (500, 1000ml/min) and liquid hourly space velocity (0.1, 0.3, 0.7, 1 h^{-1}).

The exit gas flow rate in milliliters per minute (ml/min) was monitored by an Agilent gas flow meter. Products exiting from the packed-bed reactor were cooled in the condenser and the liquid products were collected in a sampling bottle at 2 h intervals. Periodic gas sampling was also performed every 2 h using Tedlar sampling bags. For one best performing feedstock gas analysis, yields (AF, OF, gas), hydrogen consumption and hydrogen conversion were reported. The collected liquid products were centrifuged for 1 h to separate the aqueous fraction (AF) and organic fraction or hydrocarbon fraction (OFor HCF). The experiments were performed till a period of pressure difference was observed between top and bottom pressure gauges of the reactor. Table 6.1 describes the numbered components of the continuous packed-bed reactor provided in Figure 6.1, Figure 6.2a and Figure 6.2b. Figure 6.2. shows the method of catalyst loading in

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continuous packed-bed reactor (a. Method of catalyst loading inside the reactor, enclosed in a furnace b. Inside reactor with loaded catalyst).

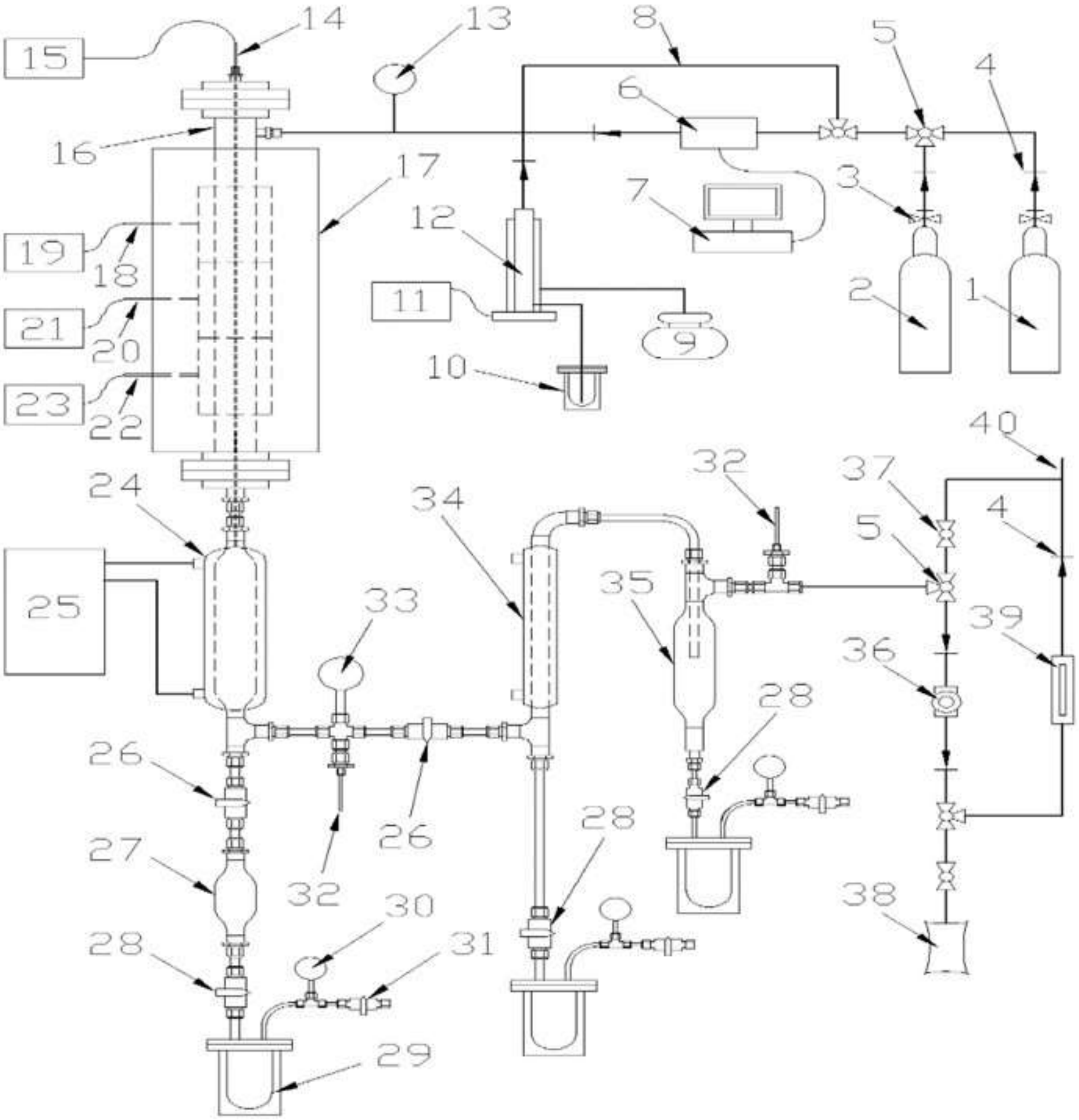

Figure 6.1 Schematic of the continuous packed-bed reactor.

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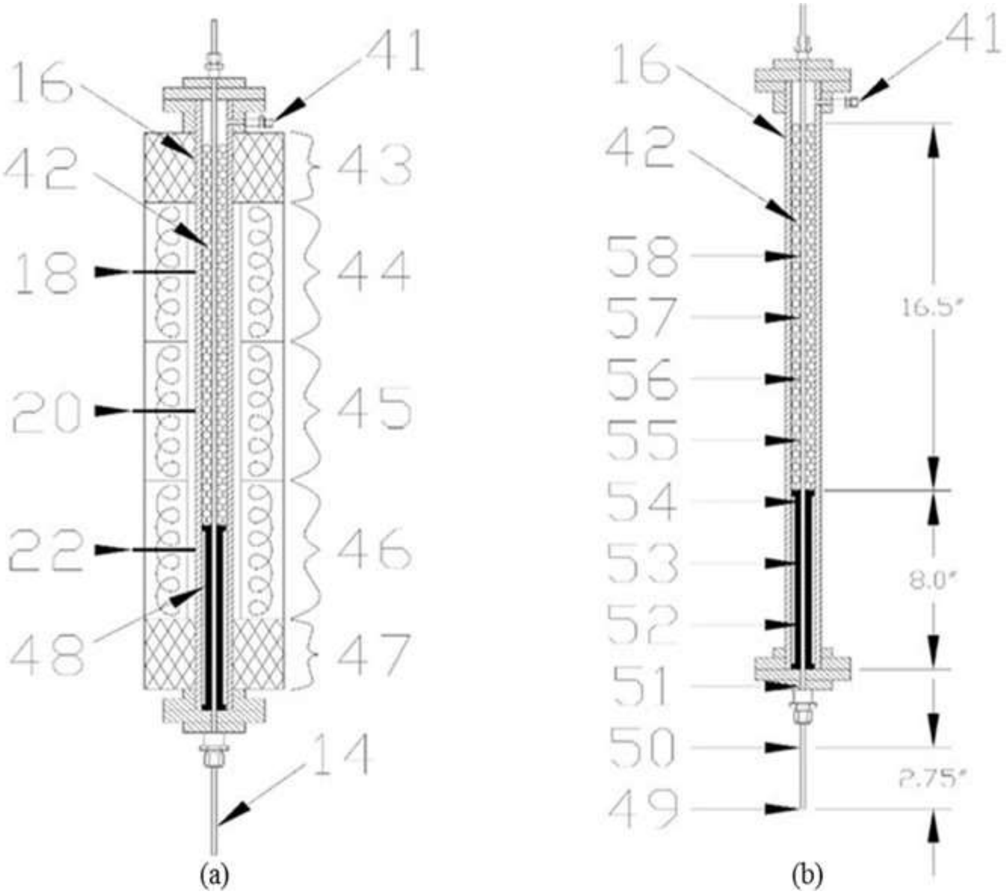

Figure 6.2 Method of catalyst loading in continuous packed-bed reactor

(a. Method of catalyst loading inside the reactor, enclosed in a furnace b. inside reactor with loaded catalyst).

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Table 6.1 The numbered components of the continuous packed-bed reactor provided in Figure 6.1 and Figure 6.2 (6.2a and b).

1	Hydrogen cylinder	30	Sampling vessel pressure gauge
2	Air cylinder	31	Sampling vessel ball valve
3	Cylinder regulator	32	Thermocouple
4	Check valve	33	Reactor exit pressure gauge
5	Three-way valve	34	Condenser 2
6	Mass flow controller (MFC)	35	Condenser 3
7	Computer-MFC program	36	Back pressure regulator
8	MFC bypass line	37	Needle valve
9	Air compressor	38	Gas sample bag
10	Bio-oil	39	Exit gas flow meter
11	High pressure pump controller	40	Gas exit line
12	High pressure pump	41	Bio-oil inlet
13	Reactor inlet pressure gauge	42	Catalyst
14	Ten zone reactor thermocouple	43	Heater top insulation, 3" long
15	Ten zone thermocouple monitor	44	Heater zone 1, 6" long
16	Reactor tube	45	Heater zone 2, 6" long
17	Reactor tube heater	46	Heater zone 3, 6" long
18	Heater zone 1 thermocouple	47	Heater bottom insulation, 3" long
19	Heater zone 1 controller	48	Catalyst support
20	Heater zone 2 thermocouple	49	Reactor thermocouple zone 1
21	Heater zone 2 controller	50	Reactor thermocouple zone 2
22	Heater zone 3 thermocouple	51	Reactor thermocouple zone 3
23	Heater zone 3 controller	52	Reactor thermocouple zone 4
24	Condenser 1	53	Reactor thermocouple zone 5
25	Chiller	54	Reactor thermocouple zone 6
26	Ball valve	55	Reactor thermocouple zone 7
27	Hydrocarbons storage vessel	56	Reactor thermocouple zone 8
28	Needle valve	57	Reactor thermocouple zone 9
29	Sampling vessel	58	Reactor thermocouple zone 10

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6.3.3 Physical and chemical analysis

RBO, PTBO 1 and PTBO 2 controls and the HCF produced from the hydroprocessing treatments of RBO, PTBO 1 and PTBO 2 were characterized following ASTM methods. For the AV test, 1 g of sample was dissolved in a isopropanol/water (v/v =35:65) solution and then titrated with 0.1 N NaOH to a pH of 8.5. The AV was then calculated as the required milligrams (mg) amounts of NaOH equivalent to 1 g of sample, according to ASTM D664. The HHV was determined with a Parr 6400 automatic isoperibol calorimeter according to ASTM D240. The Karl Fischer method was employed to determine water content by ASTM E203 with a Cole-Parmer Model C-25800-10 titration apparatus. Elemental analysis (CHNO) for determination of percent carbon (C) percent hydrogen (H), percent nitrogen (N) and percent oxygen (O) were determined by EAI CE-440 elemental analyzer, with oxygen content determined by difference by the ASTM D5291 method. The one best-performing feedstock was selected based on lowest oxygen content in their deoxygenated products. Based on the significantly superior peformance of the feedstock, one best-performing feedstock will be chosen for more detailed analysis. Product analysis was by gas chromatography mass spectroscopy (GC-MS) and scanning electron microscopy (SEM) analysis.

6.3.4 Experimental design

Each experiment was performed following 3 replicates. A factorial arrangement of treatments in a completely randomized design was employed with the one factorial being time interval or run time. The analysis of the OF properties produced following deactivation (initial run), first regeneration and second regneration was performed by application of Eq’s. 6.1, 6.2 and 6.3 with SAS software version 9.3. The analysis of

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variance (ANOVA) model as shown in Eq's. 6.1, 6.2 and 6.3 was comprised of one factorial representing run time following with deactivation, first regeneration and second regeneration for raw bio-oil (RBO 0), pretreated bio-oil 1 (PTBO 1) and pretreated bio-oil 2 (PTBO 2) to determine their influence on physical properties of AV, HHV, oxygen content and WC. ANOVA Eq's. 6.1, 6.2 and 6.3 was also applied to yield analysis. The ANOVA results showed that the main effect of time interval treatments were significant at the 0.05 level of significance for all physical properties as well as for run time intervals and yields. The ANOVA treatment significance satisfied the requirement of Fisher's protected LSD (Steel et al. 1980). The least significant difference (LSD) test was performed to separate the physical property means, run times and yields (TY, OF and AF) as influenced by the run time interval treatments.

The ANOVA model was performed for each of the physical properties, run time and liquid yields.

$$Y_i = \beta_0 + \beta_1 A_i + e_i \qquad \text{Eq.6.1}$$

Where:

Y_i represents dependent variable physical or chemical testing values: acid value, HHV, oxygen percent, WC, run time and yields,

β_0 represents the intercept term,

$\beta_1 A_i$ represents the influence of time intervals following initial run with fresh sulfided CoMo/γ-Al_2O_3 catalyst (2, 4, 6, 8, 10 and 11.0 h) for raw bio-oil (RBO 0), (2, 4, 6, 8, 10 and 12.1 h) for pretreated bio-oil 1 (PTBO 1) and time intervals (2, 4, 6, 8, 10, 12, 14, 16, 18 and 19.2 h) for pretreated bio-oil 2 (PTBO 2),

e_i represents random error term.

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The ANOVA model was performed for each of the physical properties, run time and liquid yields.

$$Y_i = \beta_0 + \beta_1 A_i + e_i \qquad \text{Eq.6.2}$$

Where:

Y_i represents dependent variable physical or chemical testing values: acid value, HHV, oxygen percent, WC, run time and yields,

β_0 represents the intercept term,

$\beta_1 A_i$ represents the influence of time intervals following first regeneration of the catalyst (2, 4, 6, and 7.1 h) for raw bio-oil (RBO 0), (2, 4, 6 and 8.5 h) for pretreated bio-oil 1 (PTBO 1) and time intervals (2, 4, 6, 8, 10 and 12.2 h) for pretreated bio-oil 2 (PTBO 2),

e_i represents random error term.

The ANOVA model was performed for each of the physical properties, run time and liquid yields.

$$Y_i = \beta_0 + \beta_1 A_i + e_i \qquad \text{Eq. 6.3}$$

Where:

Y_i represents dependent variable physical or chemical testing values: acid value, HHV, oxygen percent, WC, run time and yields,

β_0 represents the intercept term,

$\beta_1 A_i$ represents the influence of time intervals following second regeneration of the catalyst (2, 4, 6, 8 and 10.0 h) for raw bio-oil (RBO 0), (2, 4, 6, 8 and 10.0 h) for

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pretreated bio-oil 1 (PTBO 1) and time intervals (2, 4, 6, 8, 10, 12, 14 and 16.5 h) for pretreated bio-oil 2 (PTBO 2),

e_i represents random error term.

The effect of time intervals means were compared by the LSD comparison of means method performed for each of the physical properties (AV, HHV, oxygen content and WC); runtimes and yields (total yields (TY, AF and OF)) were also independently tested by LSD method. The 3 replicate values of each treatment were included in the test to determine the influence of effect of time on properties, run times and yields. Following Fisher's protected LSD test for ANOVA significance multiple comparison of means were performed by LSD for each physical property (AV, HHV, WC, oxygen content). Run times and yields were also tested in an ANOVA with Fisher's protected LSD test performed to determine significance.

6.4 Results and discussion

6.4.1 Deactivation studies

6.4.1.1 Catalyst deactivation studies with sulfided CoMo/γ-Al_2O_3 catalyst

Based on the results of the eleven process conditions tested, one was selected as the best. A temperature range of 375-400 °C, hydrogen pressure of 1500 psig, hydrogen flow rate of 1000 ml/min and liquid hourly space velocity of 0.3 h^{-1} were chosen as the best experimental operating conditions. Deactivation studies were performed at these experimental conditions to determine the longevity of the sulfided CoMo/γ-Al_2O_3 catalyst. The OF product from the treated RBO 0, PTBO 1 and PTBO 2 were compared with untreated control samples of RBO 0, PTBO 1 and PTBO 2. RBO was raw bio-oil, PTBO 1 was pretreated bio-oil without butyric anhydride treatment and PTBO 2 was

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pretreated bio-oil with butyric anhydride treatment. The physical properties of AV, HHV, oxygen content and WC were compared for three run times of 11.0 h, 12.1 h and 19.2 h. Intermediate properties over total run times were also determined at 2 h intervals to determine catalyst performance over time. All liquid yields (TY, OF and AF) for the treated OF products were compared among RBO 0, PTBO 1 and PTBO 2.

A detailed description of the reactor, the CoMo/γ-Al_2O_3 sulfiding process, and a description of the hydroprocessing and chemical analysis methods were provided in the 6.3 section of this chapter and will not be repeated here.

The properties of AV, HHV, oxygen content and WC of the treated products are described in Tables 6.2, 6.3 and 6.4. Different run times in Table 6.2, 6.3 and 6.4 indicate that the hydroprocesssing experiments were performed with varied time periods. The total run time chosen depended on two factors: 1) sudden pressure drop in the reactor due to blockage of catalyst pores and 2) a darker color indicating increased oxygen content due to deactivated catalyst. Specimens of the OF products from RBO 1, PTBO 1and PTBO 2 were collected for analyses every 2 h and at treatment end to determine change in OF properties over time.

Table 6.2 gives the mean values of the AV, HHV, oxygen content and WC percentage of the OF product from treated RBO 0 by hydroprocessing. Letters in parentheses indicate significant differences between property means as influenced by time interval. The mean AV values for RBO 0 treatments measured at 2, 4, 6, 8, 10 and 11.0 h intervals, all differed significantly. The time interval values were 96.8 to 0.5, 0.6, 0.8, 1.7, 2.8 and 3.2 mg KOH/g, respectively. These values are all much lower than the AV of control RBO 0. Table 6.2 results show that the mean AV values increased

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consistently with increased run time. In addition, the comparison of mean results show that for each periodic interval and final run time, each of the AV means increased significantly for the tested RBO 0 OF products.

Table 6.2 Mean values of the AV, HHV, oxygen content and WC percentage of the OF product from treated RBO 0 by hydroprocessing.

Properties	OF property means for each time interval tested						
	Control RBO 0	2 h	4 h	6 h	8 h	10 h	11.0 h
AV mg KOH/g	96.8 (A)	0.5 (G)	0.6 (F)	0.8 (E)	1.7 (D)	2.8 (C)	3.2 (B)
HHV MJ/Kg	16.5 (G)	44.7 (A)	43.3 (B)	43.2 (C)	43.1 (D)	40.9 (E)	40.8 (F)
Oxygen content (%)	54.5 (A)	0.2 (G)	1.4 (F)	2.1 (E)	2.5 (D)	3.1 (C)	3.9 (B)
WC (%)	29.8 (A)	0.1 (F)	0.2 (E)	0.4 (D)	0.5 (C)	0.5 (C)	2.6 (B)

Letters in parentheses indicate significant differences between property means as influenced by time interval.

The mean HHV’s for RBO 0 treatments measured at 2, 4, 6, 8, 10 and 11.0 h intervals increased from 16.5 to 44.7, 43.3, 43.2, 43.1, 40.9 and 40.8 MJ/Kg respectively. The increase in HHV was approximately 2.5 to 3 times higher than for HHV of the 16.5MJ/Kg value for raw bio-oil for all periodic interval of OF products. The mean HHV’s for time intervals decreased with time. Measuring that run time and HHV were inversely related. The comparison of mean results shows that each decrease in HHV was significant as the time interval increased.

The mean oxygen content for RBO 0 treatments measured at 2, 4, 6, 8, 10 and 11.0 h intervals increased from 54.5 to 0.2, 1.4, 2.1, 2.5, 3.1 and 3.9% respectively. These values are all much lower than for the RBO 0 control which had a value of 54.5%. The oxygen content for time intervals increased with increased run time. The comparison of

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mean results shows that each increase in oxygen content was significant as the time interval increased.

The mean WC percentages for RBO 0 treatments measured at 2, 4, 6, 8, 10 and 11.0 h intervals were 0.1, 0.2, 0.4, 0.5, 0.5 and 2.6%, respectively. Again the OF values from the treated RBO 0 raw bio-oil control had a value of 29.8%. As shown in Table 6.2, the WC percentage increased with increased run time. In addition, the conversion of mean results show that for each periodic interval and final run time, each of the water content means decreased significantly for the tested RBO 0 OF products.

Table 6.3 gives the mean values of the AV, HHV, oxygen content and WC percentage to analyze the effect of time interval (2, 4, 6, 8, 10 and 12.1 h) for PTBO 1 treatments on hydroprocessing. Letters in parentheses indicate significant differences between property means as influenced by time interval.

Table 6.3 Mean values of the AV, HHV, oxygen content and WC percentage to analyze the effect of time interval (2, 4, 6, 8, 10 and 12.1 h) for PTBO 1 treatments on hydroprocessing.

Control PTBO 1		OF property means for each time interval tested					
Property		2 h	4 h	6 h	8 h	10 h	12.1 h
AV mg KOH/g	147.2 (A)	0.3 (G)	0.5 (F)	0.6 (E)	1.5 (D)	2.6 (C)	3.1 (B)
HHV MJ/Kg	16.0 (F)	44.3 (A)	44.3 (A)	44.0 (B)	43.6 (C)	43.4 (D)	41.3 (E)
Oxygen content (%)	62.8 (A)	2.4 (G)	2.5 (F)	2.8 (E)	2.9 (D)	3.1 (C)	3.4 (B)
WC (%)	36.9 (A)	0.1 (F)	0.1 (F)	0.2 (E)	0.4 (D)	0.6 (C)	0.9 (B)

Letters in parentheses indicate significant differences between property means as influenced by time interval type

The mean AV for PTBO 1 treatments measured at 2, 4, 6, 8, 10 and 12.1 h intervals decreased from 147.2 to 0.3, 0.5, 0.6, 1.5, 2.6 and 3.1 mg KOH/g respectively.

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The mean AV values differed significantly from each other. These values are all much lower than the AV (147.2 mg KOH/g) of control PTBO 1. The mean AV values for early time intervals show lower AV values than for later time intervals. Table 6.3 results also show that the mean AV values increased with increased run time. In addition, the conversion of mean results show that for each periodic interval and final run time, each of the AV means increased significantly for the tested PTBO 1 OF products.

The mean HHV for PTBO 1 treatments at time intervals of 2, 4, 6, 8, 10 and 12.1 h increased from 16.0 to 44.3, 44.3, 43.0, 43.6, 43.4 and 41.3 MJ/Kg, respectively. The increase in HHV was approximately 2.5 to 3 times higher than for HHV of PTBO 1 for all periodic intervals of OF products. The mean HHV's for time intervals decreased with time. The comparison of mean results shows that each decrease in HHV was significant as the time interval increased with the exception of 2 and 4 h run times.

The mean oxygen content for PTBO 1 treatments measured at 2, 4, 6, 8, 10 and 12.1 h intervals increased from 62.8 to 2.4, 2.5, 2.8, 2.9, 3.1 and 3.4% respectively. The mean oxygen content for initial time intervals was lower than for later time intervals as it is evident from Table 6.3. The oxygen content for time intervals increased with increased run time. The comparison of mean results shows that each decrease in oxygen content was significant as time interval increased.

The mean WC percentages PTBO 1 treatments measured at 2, 4, 6, 8, 10 and 12.1 h intervals decreased from 36.9 to 0.1, 0.1, 0.2, 0.4, 0.6 and 0.9% respectively. The mean WC percentage for early time intervals shows lower WC percentage than for later time intervals. Table 6.3 results also show that the mean WC percentage increased with increased run time. In addition, the conversion of mean results shows that for each

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periodic interval and final run time, each of the WC percentage increased significantly for the tested PTBO 1 OF products with the exception of 2 and 4 h run times.

Table 6.4 gives the mean values of the AV, HHV, oxygen content and WC percentage to analyze the effect of time interval (2, 4, 6, 8, 10, 12, 16, 18 and 19.2 h) for PTBO 2 treatments on hydroprocessing. Letters in parentheses indicate significant differences between property means as influenced by time interval type.

The mean AV for PTBO 2 treatments measured at 2, 4, 6, 8, 10, 12, 16, 18 and 19.2 h intervals decreased significantly from 266.4 to 0.1, 0.3, 0.5, 0.6, 0.8, 1.2, 1.5, 2.3, 2.7 and 3.0 mg KOH/g respectively. The mean AV values differed significantly from each other. These values are all much lower than the AV (266.4 mg KOH/g) of control PTBO 2. The mean AV values for early time intervals show lower AV values than for later time intervals. Table 6.4 results also show that the mean AV values increased with increased run time. In addition, the conversion of mean results show that for each periodic interval and final run time, each of the AV means increased significantly for the tested PTBO 2 OF products.

The mean HHV for PTBO 2 treatments measured at 2, 4, 6, 8, 10, 12, 16, 18 and 19.2 h intervals increased from 17.5 to 43.4, 43.4, 43.2, 43.1, 43.0, 42.9, 42.8, 42.5, 42.3 and 41.5 MJ/Kg, respectively, the increase in HHV was approximately 2.5 to 3 times higher than for HHV of PTBO 2 for all periodic intervals of OF products. The mean HHV’s for time intervals decreased with time. The comparison of mean results shows that each decrease in HHV was significant as time interval increased with the exception of 2 and 4 h run times.

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Table 6.4 The mean values of the AV, HHV, oxygen content and WC percentage to analyze the effect of time interval (2, 4, 6, 8, 10, 12, 16, 18 and 19.2 h) for PTBO 2 treatments on hydroprocessing.

Control PTBO 2		OF property means for each time interval tested									
Property		2 h	4 h	6 h	8h	10h	12 h	14 h	16 h	18 h	19.2 h
AV mg KOH/g	266.4 (A)	0.1 (K)	0.3 (J)	0.5 (I)	0.6 (H)	0.8 (G)	1.2 (F)	1.5 (E)	2.3 (D)	2.7 (C)	3.0 (B)
HHV MJ/Kg	17.5 (J)	43.4 (A)	43.4 (A)	43.2 (B)	43.1 (C)	43.0 (D)	42.9 (E)	42.8 (F)	42.5 (G)	42.3 (H)	41.5 (I)
Oxygen content (%)	51.6 (A)	0 (J)	0 (J)	0.5 (I)	1.5 (H)	1.6 (G)	1.7 (F)	1.9 (E)	2.0 (D)	2.1 (C)	2.3 (B)
WC (%)	23.3 (A)	0 (J)	0 (J)	0.01 (I)	0.02 (H)	0.04 (G)	0.06 (F)	0.07 (E)	0.08 (D)	0.1 (C)	0.3 (B)

Letters in parentheses indicate significant differences between property means as influenced by time interval type.

The mean oxygen content PTBO 2 treatments measured at 2, 4, 6, 8, 10, 12, 16, 18 and 19.2 h intervals were increased from 51.6 to 0, 0, 0.5, 1.5, 1.6, 1.7, 1.9, 2.0, 2.1 and 2.3% respectively. The mean oxygen content for initial time intervals was lower than for later time intervals as it is evident from Table 6.4. The oxygen content for time intervals increased with increased run time. The comparison of mean results shows that each decrease in oxygen content was significant as time interval increased with the exception of 2 and 4 h run times.

The mean WC percentages for PTBO 2 treatments measured at time intervals of 2, 4, 6, 8, 10, 12, 16, 18 and 19.2 h decreased from 23.3 to 0, 0, 0.01, 0.02, 0.04, 0.06, 0.07, 0.08, 0.08, 0.1 and 0.3% respectively. The mean WC percentage for early time intervals show lower WC percentage than for later time intervals. Table 6.4 results also show that the mean WC percentage increased with increased run time. In addition, the conversion of mean results show that for each periodic interval and final run time, each of

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the WC percentage increased significantly for the tested PTBO 2 OF products with the exception of 2 and 4 h run times.

The intermediate OF properties produced by the time intervals of Table’s 6.2, 6.3 and 6.4 are of interest and have been discussed. The most pertinent information with regard to OF properties produced from hydroprocessing RBO 0, PTBO 1, PTBO 2 was at the end of the total run times.

6.4.2 Regeneration studies

6.4.2.1 Catalyst regeneration studies with sulfided CoMo/γ-Al_2O_3 catalyst

The catalysts applied in the regeneration studies were regenerated after the initial run times performed with fresh CoMo//γ-Al_2O_3 catalyst during the deactivation studies. In all references to regeneration it is assumed that the catalysts were also re-sulfided and this description will not be repeated. As previously described the initial total run times were 11.0 h for RBO 0, 12.1 h for PTBO 1 and 19.2 h for PTBO 2. Following these initial runs the catalysts were regenerated and re-sulfided as described in the methods section. The catalysts were then applied to each feedstock for a time period dependent on the occurance of sudden pressure drop of 40 to 50 psig in the reactor due to blockage of catalyst pores. Reactions were halted at this point. For the regeneration studies, as for the deactivation studies, specimens of each feedstock were sampled at 2 h intervals of time and at final total run time. Three replications were performed for each feedstock (RBO 0, PTBO 1, and PTBO 2).

Table 6.5 gives the mean values of the AV, HHV, oxygen content and WC percentage of the OF product from RBO 0 hydroprocessing treatment following first regeneration of the CoMo/γ-Al_2O_3 catalyst from initial run. Letters in parentheses

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indicate significant differences between property means as influenced by time interval. The mean AV values of the OF product from RBO 0 treatments measured following the first regeneration and re-sulfiding of the CoMo/γ-Al_2O_3 catalyst at 2, 4, 6 and 7.1 h intervals, all differed significantly. The time interval AV values were 0.3, 0.5, 1.1 and 3.2 mg KOH/g, respectively. These values are all much lower than the AV of control RBO 0 (96.8 mg KOH/g). Table 6.5 comparison of means results shows that for each periodic interval and final run time, each of the AV means increased significantly for the tested RBO 0 OF products.

Table 6.5 Mean values of the AV, HHV, oxygen content and WC percentage of the OF product from treated RBO 0 by hydroprocessing on first regeneration of the sulfided CoMo/γ-Al_2O_3 catalyst.

Properties		OF property means for each time interval tested			
	Control RBO 0	2 h	4 h	6 h	7.1 h
AV mg KOH/g	96.8 (A)	0.3 (E)	0.5 (D)	1.1 (C)	3.2 (B)
HHV MJ/Kg	16.5 (E)	44.3 (A)	43.3 (B)	42.4 (C)	40.1 (D)
Oxygen content (%)	54.5 (A)	0.5 (E)	0.7 (D)	1.3 (C)	4.1 (B)
WC (%)	29.8 (A)	0.2 (E)	0.3 (D)	0.4 (C)	2.7 (B)

Letters in parentheses indicate significant differences between property means as influenced by time interval type.

The mean HHV’s for RBO 0 treatments measured at 2, 4, 6 and 7.1 h were 44.3, 43.3, 42.4 and 40.1 MJ/Kg, respectively; the increase in HHV was approximately 2.5 to 3 times higher than the HHV of 16.5 MJ/Kg value for RBO 0 for all periodic intervals of OF products. The mean HHV’s for time intervals decreased with time. The comparison of means results shows that each decrease in HHV was significant as time interval increased.

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The mean oxygen content for RBO 0 treatments measured at 2, 4, 6 and 7.1 h intervals was 0.5, 0.7, 1.3 and 4.1% respectively. These values are all much lower than for the RBO 0 control which had a value of 54.5%. The comparison of means results show that for each increasing time interval oxygen content increased and that these increases in oxygen content were significant as time interval increased.

The mean WC percentages for RBO 0 treatments measured at 2, 4, 6 and 7.1 h intervals were 0.2, 0.3, 0.4 and 2.7%, respectively. These were much lower than the 29.8% WC value of the control RBO 0. As shown in Table 6.5, the WC percentage increased with increased run time. In addition, the comparison of means results show that for each periodic interval WC means increased significantly.

Table 6.6 gives the mean values of the AV, HHV, oxygen content and WC percentage of the OF product from treated RBO 0 by hydroprocessing following the second regeneration and re-sulfided of the CoMo/γ-Al_2O_3 catalyst. Letters in parentheses indicate significant differences between property means as influenced by time interval.

The presentation Table between regeneration 2 results is not to allow comparison between time interval results between regeneration 1 (Table 6.5) and regeneration 2 (Table 6.6). The purpose is to show the continued activity of the catalyst after regeneration. Because the number of time intervals for each regeneration run differed, comparison beteween time intervals was not possible. However, comparison between OF properties and total run time is appropriate and this comparison is provided in Table 1B.

The mean AV values for RBO 0 treatments measured following the first regeneration were 2, 4, 6, 8 and 10 h, intervals, and all differed significantly. The time interval AV values were 0.3, 0.5, 1.9, 2.3 and 3.7 mg KOH/g, respectively. These values

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are all much lower than the AV of the control RBO 0 (96.8 mg KOH/g). Table 6.6, comparison of means results shows that for each periodic interval, each of the AV means increased significantly for the tested RBO 0 OF products.

Table 6.6 Mean values of the AV, HHV, oxygen content and WC percentage of the OF product from treated RBO 0 by hydroprocessing on second regeneration of the sulfided CoMo/γ-Al_2O_3 catalyst.

Properties		OF property means for each time interval tested				
	Control RBO 0	2 h	4 h	6 h	8 h	10 h
AV mg KOH/g	96.8 (A)	0.3 (F)	0.5 (E)	1.9 (D)	2.3 (C)	3.7 (B)
HHV MJ/Kg	16.5 (F)	44.8 (A)	43.5 (B)	41.8 (C)	41.1 (D)	40.0 (E)
Oxygen content (%)	54.5 (A)	0.3 (F)	1.5 (E)	2.0 (D)	4.5 (C)	5.3 (B)
WC (%)	29.8 (A)	0.2 (F)	0.4 (E)	0.6 (D)	1.9 (C)	4.4 (B)

Letters in parentheses indicate significant differences between property means as influenced by time interval.

The mean HHV's for RBO 0 treatments measured at 2, 4, 6, 8 and 10 h intervals were 44.8, 43.5, 41.8, 41.1 and 40.0 MJ/Kg respectively; the increase in HHV was approximately 2.5 to 3 times higher than the HHV of 16.5 MJ/Kg value for the raw bio-oil RBO 0 control for all of OF products tested at periodic intervals. The mean HHV's for time intervals decreased with time. The comparison of means results shows that each decrease in HHV was significant for each increasing time interval.

The mean oxygen content for RBO 0 treatments measured at 2, 4, 6, 8 and 10 h intervals was 0.3, 1.5, 2.0, 4.5 and 5.3%, respectively. These values are all much lower than for the RBO 0 control which had a value of 54.5%. The comparison of means results shows that for each increasing time interval and final run time the oxygen content increased significantly.

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The mean WC percentages for RBO 0 treatments measured at 2, 4, 6, 8 and 10 h intervals were 0.2, 0.4, 0.6, 1.9 and 4.4% respectively. These were much lower than the 29.8% WC value of the control RBO 0. As shown in Table 6.6, the WC percentage increased with increased run time. In addition, the comparison of means results show that for each periodic interval, each of the WC means increased significantly.

Table 6.7 decribes the yields including TY, OF and AF for treated RBO 0 for initial (11.0 h), first and second regeneration plus re-sulfidation (7.1 and 10.0 h). The TY yields obtained with RBO 0 treatment for initial, first and second regeneration were 76.8, 78.2 and 80.1 wt%, respectively. Each of the regeneration 1, feedstock yield percentages differed significantly among themselves. The treated OF yields for initial, first and second regeneration were 16.4, 14.1 and 24.8 wt%, respectively and the treated AF yields for initial, first and second regeneration were 60.4, 64.1 and 64.9 wt%, respectively. From the tested treatments second regeneration treatment yielded the significantly lowest AF yields of 52.3 wt% and significantly higher OF yields of 24.8 wt%.

Table 6.7 Comparison of means for yields (TL, OF and AF) for feedstock RBO 0 for initial run, regeneration 1 and regeneration 2 total run times.

Yields RBO 0 (%)	Initial run (11.0 h)	Regeneration 1 (7.1 h)	Regeneration 2 (10.0 h)
TY	76.8 (C)	78.2 (B)	80.1 (A)
OF	16.4 (B)	14.1 (C)	24.8 (A)
AF	60.4 (B)	64.1 (A)	55.3 (C)

Letters in parentheses indicate significant differences between property means as influenced by time interval.

Table 6.8 gives the comparison of elemental analysis (CHNOS%) of fresh, sulfided and spent CoMo/γ-Al_2O_3 catalyst from intial run (IR), first regeneration or

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regeneration 1(R1) and second regeneration or regeneration 2 (R2). The CHNOS properties of fresh CoMo/Al_2O_3 catalyst were 0.03, 0.65, 0.02, 99.3 and 0.59 % respectively. The CHNOS properties of sulfided CoMo/Al_2O_3 catalyst were 1.45, 0.74, 0, 97.81 and 3.51 % respectively. The CHNOS properties of spent CoMo/Al_2O_3 catalyst from IR were 32.99, 1.96, 0.2, 64.85 and 1.47 % respectively. The CHNOS properties of spent CoMo/Al_2O_3 catalyst from R1 were 17.99, 0.84, 0, 81.17 and 2.11 % respectively. The CHNOS properties of spent CoMo/Al_2O_3 catalyst from R2 were 5.19, 0.2, 0, 94.61 and 2.15 % respectively.

For comparison purposes controls for fresh, sulfided and spent regenerated CoMo/γ-Al_2O_3 catalysts were produced to allow accurate comparison of carbon and sulfur content.The results given in Table 6.8 indicate that the carbon content of the spent CoMo/γ-Al_2O_3 catalyst for IR, R1 and R2 decreased gradually. The decrease in run time (7.1 h) and low OF yields (14.1 %) for R1 compared to the IR was due to increased carbon/coke deposition (32.99%) and reduced %O (64.85%) on catalyst surface. Bycontrast, the increase in run time after spent R2 was due to less coke deposition (17.99%) and as a result of higher oxygen (81.17%) on catalyst surface than R1. Though the run time and yields were increased for regeneration 2 the quality of OF (hydrocarbon percentage) was not as good as the OF intial run, which is evident from below Table 6.9.

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Table 6.8 Elemental analysis (CHNOS%) of fresh, sulfided and spent IR, R1 and R2 CoMo/γ-Al_2O_3 catalysts at run time end.

Values at final run time					
Catalyt type	%C	%H	%N	%O	%S
Fresh CoMo/γ-Al_2O_3	0.03	0.65	0.02	99.3	0.59
Sulfided CoMo/γ-Al_2O_3	1.45	0.74	0	97.81	3.51
RBO 0 IR	32.99	1.96	0.2	64.85	1.47
RBO 0 R1	17.99	0.84	0	81.17	2.11
RBO 0 R2	5.19	0.2	0	94.61	2.15

Table 6.9 GC-MS analysis (percentage of hydrocarbon (% HC)) and percentage of elemental sulfur (%S) of OF for IR, R1 and R2.

GC-MS	Wt% OF yields	%HC	%S
RBO 0	NA	0	0
RBO 0 IR	16.4	93.8	0
RBO 0 R1	14.1	90.5	0
RBO 0 R2	24.8	77.8	0

While the quality of R2 is substantially lower in hydrocarbon area percentages (HC % of 77.8 wt%), it showed the best yield of 24.8 wt% (Table 6.9). The HC percentage values for IR and R1 were high at 93.8 and 90.5%. However, their respective yields of 16.4 and 14.1 wt% were low. These results show that the catalyst activity decreases after each run.

From Tables 6.2, 6.5, and 6.6, it was observed that there was only a difference of 0.5 mg KOH/g of AV, HHV of 0.8 MJ/Kg, oxygen content of 1.4 % and WC of 1.8 % from properties of initial run to properties of OF following second regeneration. From these observations, the OF yields increased from 16.4 to 24.8% from intial run tothe

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second regeneration. This was due to less coke deposition for the second regeneration, evident from Table 6.9. Though the yields and run time increased for the second regeneration in comparison to the first regeneration, the quality of OF decreased from intial run to first regeneration and from first regeneration to second regeneration, as evident from Table 6.9 (93.8, 90.5 and 77.8% HC).

Table 6.10 gives the mean values of the AV, HHV, oxygen content and WC percentage of the OF product from treated PTBO 1 by hydroprocessing following first regeneration of the CoMo/γ-Al_2O_3 catalyst from initial run. Letters in parentheses indicate significant differences between property means as influenced by time interval. The mean AV values for PTBO 1 treatments measured at 2, 4, 6 and 8.5 h intervals, all differed significantly. These values are all much lower than the AV of control PTBO 1. The time interval AV values were 0.3, 0.5, 0.6 and 3.1 mg KOH/g, respectively. These values are much lower than the AV of control PTBO 1 (147.2 mg KOH/g). Table 6.10, comparison of means results show that for each periodic interval the AV means increased significantly for the tested PTBO 1 OF products.

The mean HHV's for PTBO 1 treatments measured at 2, 4, 6 and 8.5 h intervals increased from 16.0 to 44.6, 43.5, 43.4 and 40.6 MJ/Kg respectively. The increase in HHV was approximately 2.5 to 3 times higher than the HHV of 16.0 MJ/Kg value for the PTBO 1 control for all periodic intervals of OF products. The mean HHV's for time intervals decreased with time. The comparison of mean results shows that each decrease in HHV was significant as time interval increased.

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Table 6.10 Mean values of the AV, HHV, oxygen content and WC percentage of the OF product from treated PTBO 1 by hydroprocessing on first regeneration of the sulfided CoMo/γ-Al_2O_3 catalyst.

Property	OF property means for each time interval tested				
	Control PTBO 1	2 h	4 h	6 h	8.5 h
AV mg KOH/g	147.2 (A)	0.3 (E)	0.5 (D)	0.6 (C)	3.1 (B)
HHV MJ/Kg	16.0 (E)	44.6 (A)	43.5 (B)	43.4 (C)	40.6 (D)
Oxygen content (%)	62.8 (A)	1.1 (E)	1.4 (D)	1.8 (C)	3.5 (B)
WC (%)	36.9 (A)	0.1 (E)	0.6 (D)	0.8 (C)	1.1 (B)

Letters in parentheses indicate significant differences between property means as influenced by time interval type.

The mean oxygen content for PTBO 1 treatments measured at 2, 4, 6 and 8.5 h intervals were 1.1, 1.4, 1.8 and 3.5%, respectively. These values are all much lower than for the PTBO 1 control which had a value of 62.8%. The comparison of mean results shows that each increase in oxygen content was significant as time interval increased.

The mean WC percentages for PTBO 1 treatments measured at 2, 4, 6 and 8.5 h intervals were 0.1, 0.6, 0.8 and 1.1% respectively. These values were much lower than 36.9% WC value of the control PTBO 1. As shown in Table 6.10, the WC percentage increased with increased run time. In addition, the comparison of means results shows that for each periodic interval and final run time, each of the water content means decreased significantly.

Table 6.11 gives the mean values of the AV, HHV, oxygen content and WC percentage of the OF product from treated PTBO 1 by hydroprocessing following second regeneration of the CoMo/γ-Al_2O_3 catalyst. Letters in parentheses indicate significant differences between property means as influenced by time interval. The mean AV values for PTBO 1 treatments measured following second regeneration of CoMo/γ-Al_2O_3

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catalyst at 2, 4, 6, 8 and 10 h intervals, all differed significantly. The time interval AV values were 0.2, 0.3, 1.1, 1.9 and 3.2 mg KOH/g, respectively. These values are all much lower than the AV of control PTBO 1 (147.2 mg KOH/g). Table 6.11, comparison of means results show that for each periodic interval and final run time, each of the AV means increased significantly for the tested PTBO 1 OF products.

Table 6.11 Mean values of the AV, HHV, oxygen content and WC percentage of the OF product from treated PTBO 1 by hydroprocessing on second regeneration of the sulfided CoMo/γ-Al_2O_3 catalyst.

Property	OF property means for each time interval tested					
	Control PTBO 1	2 h	4 h	6 h	8 h	10 h
AV mg KOH/g	147.2 (A)	0.2 (F)	0.3 (E)	1.1 (D)	1.9 (C)	3.2 (B)
HHV MJ/Kg	16.0 (F)	44.2 (A)	43.4 (B)	42.5 (C)	41.2 (D)	40.1 (E)
Oxygen content (%)	62.8 (A)	0.1 (F)	1.5 (E)	1.8(D)	3.4 (C)	5.2 (B)
WC (%)	36.9 (A)	0.1 (F)	0.6 (E)	0.8 (D)	1.5 (C)	4.1 (B)

Letters in parentheses indicate significant differences between property means as influenced by time interval type.

The mean HHV's for PTBO 1 treatments measured at 2, 4, 6, 8 and 10 h intervals were 44.2, 43.4, 42.5, 41.2 and 40.1 MJ/Kg respectively. The increase in HHV was approximately 2.5 to 3 times higher than the HHV of 16.0 MJ/Kg value for PTBO 1 control for all periodic intervals of OF products. The mean HHV's for time intervals decreased with time. The comparison of means results shows that each decrease in HHV was significant as time interval increased.

The mean oxygen content for PTBO 1 treatments measured at 2, 4, 6, 8 and 10 h intervals was 0.1, 1.5, 3.4 and 5.2%, respectively. These values are all much lower than for the PTBO 1 control which had a value of 62.8%. The oxygen content for time

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intervals increased with increased run time. The comparison of means results shows that each increase in oxygen content was significant as time interval increased.

The mean WC percentages for PTBO 1 treatments measured at 2, 4, 6, 8 and 10 h intervals were 0.1, 0.6, 0.8, 1.5and 4.1% respectively. These were lower than the PTBO 1 control which had a value of 36.9%. As shown in Table 6.11, the WC percentage increased with increased run time. In addition, the conversion of means results shows that for each periodic interval WC means increased significantly.

Table 6.12 Yields (TL, OF and AF) for feedstock for PTBO 1 by hydroprocessing treatments.

Yields PTBO 1 (%)	Initial run (12.1)	Regeneration1 (10.0)	Regeneration 2 (10.0)
TY	86.1 (A)	73.7 (B)	71.0 (C)
OF	18.7 (B)	10.4 (C)	21.5 (A)
AF	67.4 (A)	63.3 (B)	50.5 (C)

Table 6.12 decribes the yields including TY, OF and AF for treated PTBO 1 for initial (12.2 h), first and second regeneration (10.0 and 10.0 h). The TY yields obtained with PTBO 1 treatment for initial, first and second regeneration were 86.1, 73.7 and 71.0 wt% respectively. Each of the feedstock yield percentages differed significantly among themselves. The treated OF yields for initial, first and second regeneration were 18.7, 10.4 and 21.5 wt%. respectively. And the treated AF yields for initial, first and second regeneration were 67.4, 63.3 and 50.5 wt%, respectively. From the tested treatments regeneration 2 treatment yielded the significantly lowest AF yields of 50.5 wt% and significantly higher OF yields of 21.5 wt%.

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For comparison purposes controls for fresh, sulfided and spent regenerated $CoMo/Al_2O_3$ catalysts were produced to allow accurate comparison of carbon and sulfur content.The results given in Table 6.13 indicate that the carbon content of the spent $CoMo/Al_2O_3$ catalyst for IR, R1 and R2 decreased gradually. The decrease in run time (8.5 h) and low OF yields (10.4 %) for R1 compared to the IR was due to increased carbon/coke deposition (16.4%) and reduced %O (82.63%) on catalyst surface. Bycontrast, the increase in run time after spent R2 was due to less coke deposition (11.31%) and as a result of higher oxygen (87.85%) on catalyst surface than R1. Though the run time and yields were increased for regeneration 2 the quality of OF (hydrocarbon percentage) was not as good as the OF intial run, which is evident from below Table 6.13.

Table 6.13 Elemental analysis (CHNOS%) of fresh, sulfided and spent IR, R1 and R2 $CoMo/\gamma\text{-}Al_2O_3$ catalysts at run time end.

	Values at final run time				
Catalyt type	%C	%H	%N	%O	%S
Fresh $CoMo/Al_2O_3$	0.03	0.65	0.02	99.3	0.59
Sulfided $CoMo/Al_2O_3$	1.45	0.74	0	97.81	3.51
PTBO 1 IR	16.4	0.96	0.01	82.63	3.0
PTBO 1 R1	11.31	0.84	0	87.85	2.2
PTBO 1 R2	14.19	0.2	0	95.61	2.4

While the quality of R2 is substantially lower in hydrocarbon area percentages (HC % of 82.7 wt%), it showed the best yield of 24.8 wt% (Table 6.14). The HC percentage values for IR and R1 were high at 94.3 and 90.2%. However, their respective

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yields of 16.4 and 14.1 wt% were low. These results show that the catalyst activity decreases after each run.

Table 6.14 GC/MS analysis (percentage of hydrocarbon (% HC)) and percentage of elemental sulfur (%S) of OF for IR, R1 and R2.

GC/MS	Wt% OF yields	%HC	%S
PTBO 1	NA		0.5
RBO 0 IR	16.4	94.3	0
RBO 0 R1	14.1	90.2	0
RBO 0 R2	24.8	82.7	0

Table 6.15 gives the mean values of the AV, HHV, oxygen content and WC percentage of the OF product from treated PTBO 2 by hydroprocessing on first regeneration of the sulfided CoMo/γ-Al_2O_3 catalyst. Letters in parentheses indicate significant differences between property means as influenced by time interval. The mean AV values for PTBO 2 treatments measured following the first regeneration at 2, 4, 6, 8, 10 and 12.2 h intervals, all differed significantly. The time interval AV values were 0.1, 0.3, 0.5, 0.6, 0.9 and 1.3 mg KOH/g, respectively. These values are all much lower than the AV of control PTBO 1 of 266.4 mg KOH/g. Table 6.15, comparison of mean results shows that for each periodic interval and final run time, each of the AV means increased significantly for the tested PRBO 2 OF products.

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Table 6.15 Mean values of the AV, HHV, oxygen content and WC percentage of the OF product from treated PTBO 2 by hydroprocessing on first regeneration of the sulfided $CoMo/\gamma\text{-}Al_2O_3$ catalyst.

		OF property means for each time interval tested					
Property	Control PTBO 2	2 h	4 h	6 h	8 h	10 h	12.2 h
AV mg KOH/g	266.4 (A)	0.1 (G)	0.3 (F)	0.5 (E)	0.6 (D)	0.9 (C)	1.3 (B)
HHV MJ/Kg	17.5 (G)	44.4 (A)	43.2 (B)	43.0 (C)	42.9 (D)	42.6 (E)	41.4 (F)
Oxygen content (%)	51.6 (A)	0 0 (G)	0.0 (F)	1.3 (E)	1.5 (D)	1.8 (C)	2.5 (B)
WC (%)	23.3 (A)	0.1 (E)	0.1 (E)	0.3 (D)	0.5 (C)	0.3 (B)	0.3 (B)

Letters in parentheses indicate significant differences between property means as influenced by time interval type.

The mean HHV's for PTBO 2 treatments measured at 2, 4, 6, 8, 10 and 12.2 h intervals increased were 44.4, 43.2, 43.0, 42.9, 42.6 and 41.4 MJ/Kg respectively, the increase in HHV was approximately between 2.5 to 3 times was higher than the HHV of 17.5 MJ/Kg value for control PTBO 2 for all periodic interval of OF products. The comparison of means results show that each decrease in HHV was significant as time interval increased.

The mean oxygen content for PTBO 2 treatments measured at 2, 4, 6, 8, 10 and 12.2 h intervals were 0, 0, 1.3, 1.5, 1.8 and 2.5% respectively. These values are all much lower than for the PTBO 2 control which had a value of 51.6%. The comparison of means results shows that each increase in oxygen content was significant as time interval increased with the exception of 2 and 4 h.

The mean WC percentages for PTBO 2 treatments measured at 2, 4, 6, 8, 10 and 12.2 h intervals were 0.1, 0.1, 0.3, 0.5, 0.3 and 0.3% respectively. These WC values were

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much lower than the PTBO 2 control which had a value of 23.3%. As shown in Table 6.15, the WC percentage increased with increased run time. The comparison of means results show that each increase in WC was significant as time interval increased with the exception of 2 and 4 h and 8 and 10 h.

Table 6.16 gives the mean values of the AV, HHV, oxygen content and WC percentage of the OF product from treated PTBO 2 by hydroprocessing following second regeneration of the CoMo/γ-Al_2O_3 catalyst. Letters in parentheses indicate significant differences between property means as influenced by time interval. The mean AV values for PTBO 2 treatments measured following first regeneration and re-sulfidation were 2, 4, 6, 8, 10, 12, 14 and 16.5 h intervals, all differed significantly. These values are all much lower than the AV of control PTBO 2 of 266.4 mg KOH/g. The time interval.values were 0.2, 0.3, 0.5, 0.6, 0.6, 1.4, 1.5 and 1.7 mg KOH/g, respectively. Table 6.16, coomparison of means results shows that for each periodic interval and final run time, each of the AV means increased significantly.

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Table 6.16 Mean values of the AV, HHV, oxygen content and WC percentage of the OF product from treated PTBO 2 by hydroprocessing on second regeneration of the sulfided CoMo/γ-Al_2O_3 catalyst.

	OF property means for each time interval tested								
Property	Control PTBO 2	2 h	4 h	6 h	8 h	10 h	12 h	14 h	16.5 h
AV mg KOH/g	266.4 (A)	0.2 (H)	0.3 (G)	0.5 (F)	0.6 (E)	0.6 (E)	1.4 (D)	1.5 (C)	1.7 (B)
HHV MJ/Kg	17.5 (I)	43.9 (A)	43.2 (B)	43.2 (C)	42.9 (D)	42.8 (E)	41.2 (F)	41.1 (G)	40.9 (H)
Oxygen content (%)	51.6 (A)	0 (I)	1.1 (H)	1.5 (G)	1.8 (F)	2.1 (E)	2.9 (D)	3.5 (C)	4.6 (B)
WC (%)	23.3 (A)	0.1 (H)	0.3 (G)	0.4 (F)	0.5 (E)	0.5 (E)	1.5 (D)	1.8 (C)	2.9 (B)

Letters in parentheses indicate significant differences between property means as influenced by time interval type.

The mean HHV's for PTBO 2 treatments measured at 2, 4, 6, 8, 10, 12, 14 and 16.5 h intervals were 43.9, 43.2, 43.2, 42.9, 42.8, 41.2, 41.1 and 40.9 MJ/Kg, respectively. The increase in HHV was approximately 2.5 to 3 times higher than for HHV of 17.5 MJ/Kg value for control PTBO 2 for all periodic intervals of OF products. The mean HHV's for time intervals decreased with time. The comparison of means results shows that each decrease in HHV was significant as time interval increased.

The mean oxygen content for PTBO 2 treatments measured at 2, 4, 6, 8, 10, 12, 14 and 16.5 h intervals were 0, 1.1, 1.5, 1.8, 2.1, 2.9, 3.5 and 4.6%, respectively. These values are all much lower than for the PTBO 2 control which had a value of 51.6. The comparison of means results shows that each increase in oxygen content was significant as time interval increased.

The mean WC percentages for PTBO 2 treatments measured at 2, 4, 6, 8, 10, 12, 14 and 16.5 h intervals were 0.1, 0.3, 0.4, 0.5, 0.5, 1.5, 1.8, and 2.9%, respectively. These

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values were mpore lower than the PTBO 2 control which had a value of 23.3%. As shown in Table 6.16, the WC percentage increased with increased run time. The comparison of means results shows that each increase in oxygen content was significant as time interval increased with the exception of 8 and 10 h.

Table 6.17 decribes the yields including TY, OF and AF for treated PTBO 1 for initial (19.2 h), first and second regeneration (12.1 and 16.5 h). The TY yields obtained with PTBO 2 treatment for initial, first and second regeneration were 82.3, 65.0 and 71.5 wt%, respectively. Each of the feedstock yield percentages differed significantly among themselves. The treated OF yields for initial, first and second regeneration were 30.0, 16.2 and 30.5 wt% respectively and the treated AF yields for initial, first and second regeneration were 52.3, 48.8 and 41.0 wt% ,respectively. From the tested treatments regeneration 2 treatment yielded the significantly lowest AF yields of 41.0 wt% and significantly higher OF yields of 30.5 wt%.

Table 6.17 Yields (TL, OF and AF) for feedstock PTBO 1 by hydroprocessing treatments.

Yields PTBO 2 (wt %)	Initial run	Regeneration1	Regeneration 2
TY	82.3 (A)	65 (C)	71.5 (B)
OF	30.0 (B)	16.2 (C)	30.5 (A)
AF	52.3 (A)	48.8 (C)	41.0 (B)

The intermediate OF properties produced for the time intervals and final run time of Tables 6.4, 6.16 and 6.17 are of interest and have been discussed. However, the most pertinent information is the post-hydroprocessing properties of OF from RBO 0, PTBO 1, PTBO 2 produced at the termination total run times.

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For comparison purposes controls for fresh, sulfided and spent regenerated $CoMo/Al_2O_3$ catalysts were produced to allow accurate comparison of carbon and sulfur content.The results given in Table 6.18 indicate that the carbon content of the spent $CoMo/Al_2O_3$ catalyst for IR, R1 and R2 decreased gradually. The decrease in run time (12.2 h) and low OF yields (16.2 %) for R1 compared to the IR was due to increased carbon/coke deposition (18.35%) and reduced %O (80.6%) on catalyst surface. Bycontrast, the increase in run time after spent R2 was due to less coke deposition (7.2%) and as a result of higher oxygen (91.0%) on catalyst surface than R1. Though the run time and yields were increased for regeneration 2 the quality of OF (hydrocarbon percentage) was not as good as the OF intial run, which is evident from Table 6.19.

While the quality of R2 is substantially lower in hydrocarbon area percentages (HC % of 83.6 wt%), it showed the best yield of 24.8 wt% (Table 6.19). The HC percentage values for IR and R1 were high at 94.9 and 90.5%. However, their respective yields of 16.4 and 14.1 wt% were low. These results show that the catalyst activity decreases after each run.

Table 6.18 Elemental analysis (CHNOS %) of fresh, sulfided and spent IR, R1 and R2 $CoMo/\gamma\text{-}Al_2O_3$ catalysts at run time end.

	Values at final run time				
Catalyt type	%C	%H	%N	%O	%S
Fresh $CoMo/Al_2O_3$	0.03	0.65	0.02	99.3	0.59
Sulfided $CoMo/Al_2O_3$	1.45	0.74	0	97.81	3.5
PTBO 2 IR	18.35	0.96	0.09	80.6	3.1
PTBO 2 R1	7.2	0.8	0	91.0	2.5
PTBO 2 R2	3.5	0.4	0	96.1	2.7

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Table 6.19 GC-MS analysis (percentage of hydrocarbon (% HC)) and percentage of elemental sulfur (%S) of OF for IR, R1 and R2.

GC-MS	Wt% OF yields	%HC	%S
PTBO 2	NA	0.9	0.4
PTBO 2 IR	16.4	94.9	0
PTBO 2 R1	14.1	90.5	0
PTBO 2 R2	24.8	83.6	0

Table 6.20 Gas analysis of PTBO 2 at IR, R1 and R2

Sample	H_2 %	O_2 %	N_2%	CH_4 %	CO %	CO_2 %	C_2H_6 %
PTBO 2 IR	63.4	0.5	1.6	2.0	0.4	6.0	1.8
PTBO 2 R1	53.9	1.3	4.3	2.2	0.6	6.9	1.7
PTBO 2 R2	53.6	0.4	1.5	2.9	0.7	10.1	1.8

Table 6.20 shows the analysis of gas samples collected during the hydroprocessing experiments. Gas samples were collected 10-15 minutes prior to collecting the liquid samples. Gas analysis was used to interpret the H_2 percentage in the exit gas as well as the formation of low molecular weight hydrocarbon gases such as CH_4, C_2H_6, etc. As seen below in Table 6.20, exit gases from the PTBO 2 R1 and R2 experiment contained the lowest hydrogen percentage, indicating that more hydrogen was consumed for hydroprocessing PTBO 2 R1 and R2, because they are spent catalysts. The exit gases from the experiment with PTBO 2 IR had 63.4% hydrogen showed the best performance is evident from physical and chemical analysis.

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Table 6.21 Yields (OF, AF and gas), hydrogen consumption and hydrogen conversion for the PTBO 2 experiments (PTBO 2 IR, R1 and R2).

Yields on dry basis	PTBO 2 IR (units)	PTBO 2 R1 (units)	PTBO 2 R2 (units)
OF	0.43g/g feed (dry basis)	0.23g/g feed (dry basis)	0.47g/g feed (dry basis)
AF	1.0 g/g feed (dry basis)	1.2 g/g feed (dry basis)	1.0 g/g feed (dry basis)
Gas	0.83 g/g feed (dry basis)	0.59 g/g feed (dry basis)	1.5 g/g feed (dry basis)
Char	13 to 15 wt%	12 to 13 wt%	11 to 12%
Hydrogen consumption	625.9 ml/min	636.2 ml/min	624.8 ml/min
Hydrogen conversion	37.4%	36.4%	37.5%

Table 6.21 shows, for the best feedstock PTBO 2 (IR, R1 and R2) for the sulfided CoMo/γ-Al_2O_3 catalyst at a temperature of 375-400 °C, pressure of 1500 psig, liquid hourly space velocity of 0.3 h^{-1} and hydrogen flow rate of 1000 ml/min showed the yields (OF, AF and gas yields) based on dry basis were 0.43, 1.0 and 0.83 g/g feed respectively for IR, 0.23, 1.2 and 0.59 g/g feed respectively for R1 and 0.47, 1.0 and 1.5 g/g feed respectively for R2. The reason for difference in yields was explained in before section with reference to Tables 6.17, 6.18 and 6.19 and will not be repeated here.The hydrogen consumption for IR, R1 and R2 were 625.9, 636.2 and 624.8 ml/min respectively. The hydrogen conversion for IR, R1 and R2 were 37.4, 36.4 and 37.5% respectively.

6.4.3 Catalyst characterization

6.4.3.1 Scanning electron microscopy (SEM)

Catalyst morphology and superficial composition were studied by SEM-EDX using JEOL JSM 6500F field emission. SEM and the elemental data were collected and

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analysed with Oxford Instrument's X-max 50 EDS detector and INCA Energy software. The SEM images and the EDS data were obtained at 5KV and 15KV excitation voltage respectively.

SEM photographs of the fresh, sulfided and spent catalysts after 19.1 h (IR), 12.1 h (R1) and 16.5 h (R2) reaction times are shown in Figures 6.3, 6.4, 6.5, 6.6 and 6.7 the images for the fresh (Figure 6.3) and fresh sulfided catalyst (Figure 6.4) showed that most of the catalyst surfaces were covered with active sites. The images of spent CoMo/γ-Al_2O_3 catalyst after 19.2 (Figure 6.5), 12.1 (Figure 6.6) and 16.5 h (Figure 6.7) reaction times showed carbon deposition on the surface. Carbon deposition is shown as the fibrous structure on the catalyst surface. Furthermore, EDX analysis shows the presence of distribution of certain elements such as active sites Mo-S, Co, Mo and traces of other non-active elements such as Si, Mn, Mg and others.

6.4.3.2 Energy Dispersive X-ray analysis (EDX Analysis)

The EDX analysis system works as an integrated feature of SEM. The fresh, fresh sulfided and spent CoMo/γ-Al_2O_3 catalysts after 19.1 h (IR), 12.1 h (R1) and 16.5 h (R2) reaction time (catalysts from PTBO2 hydroprocessing) are shown in Figures 6.3, 6.4, 6.5, 6.6 and 6.7. These catalysts were subjected to EDX analysis to detect any change in the composition on the catalyst surface due to carbon deposition, presence and loss of active sites and other elements. The images from Figures 6.3 (fresh CoMo/γ-Al_2O_3 catalyst), and 6.4 (fresh sulfided CoMo/γ-Al_2O_3 catalyst) showed prominent peaks of MO and Mo-S. Whereas, the spent catalysts after 19.1 h (Figure 6.5) reaction time had no Mo-S peak; only a sulfur peak is present. The lack of Mo-S peak indicates that the catalyst active sites disappeared. By contrast for the spent catalysts after 12.1 h (Figure 6.6) and 16.5 h

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(Figure 6.7) reaction times, a Mo-S peak was identified but the height (intensity) of Mo-S peak was much lower. From the images of SEM with EDX analysis (Figures 6.3, 6.4, 6.5, 6.6 and 6.7), it is evident that the catalyst activity was decreasing after each run.

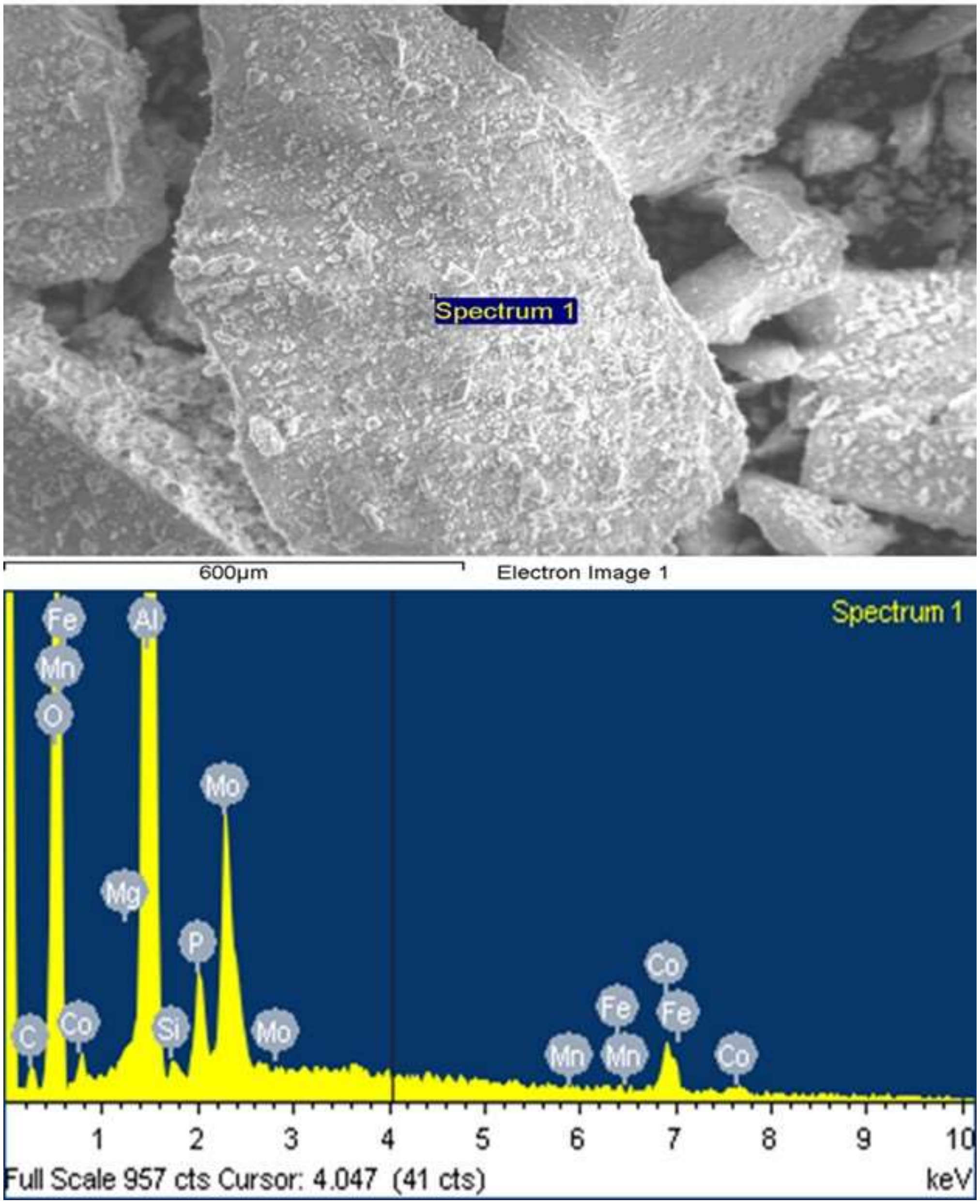

Figure 6.3 SEM with EDX analysis of fresh CoMo/γ-Al_2O_3 catalyst.

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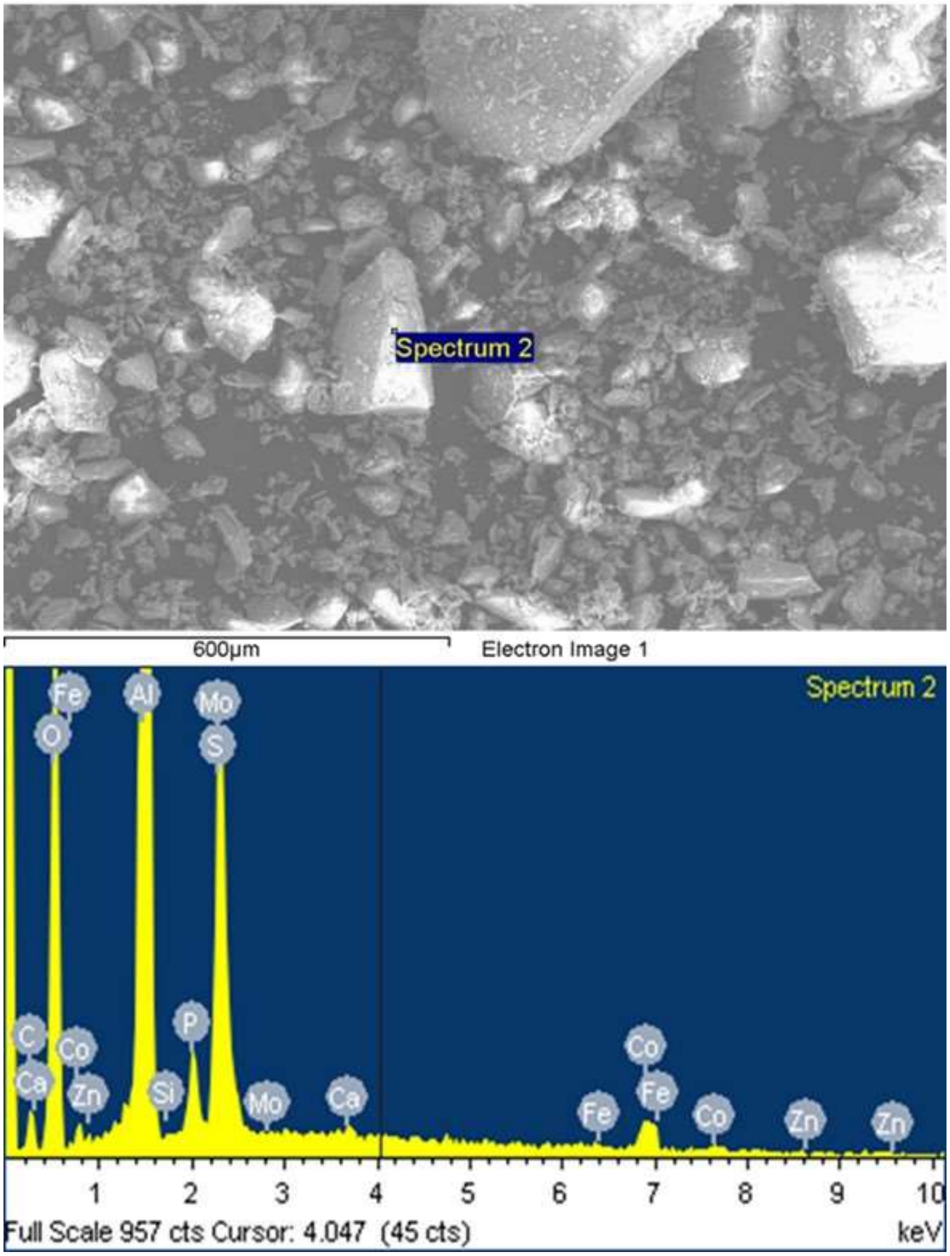

Figure 6.4 SEM with EDX analysis of sulfided CoMo/γ-Al_2O_3 catalyst.

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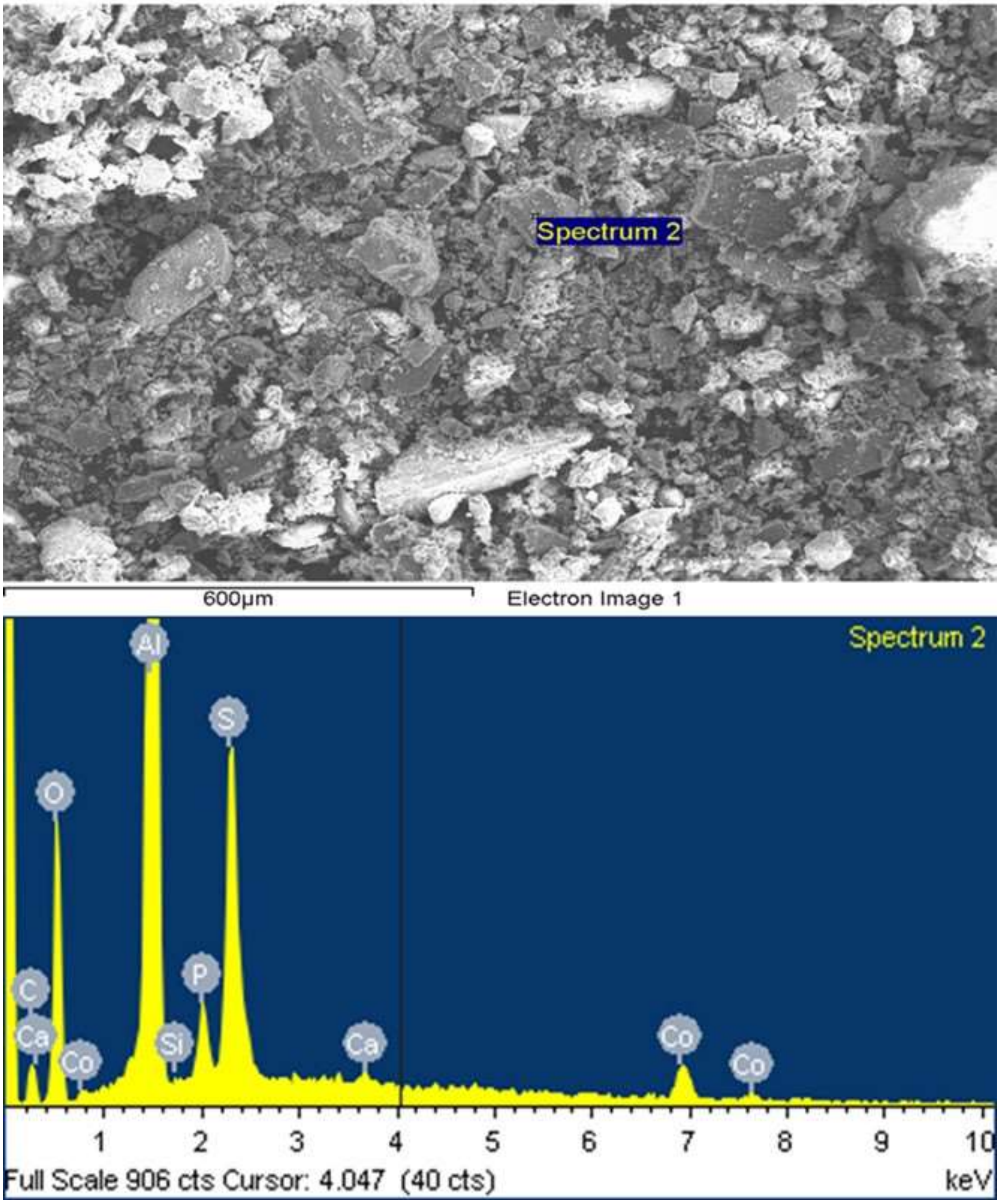

Figure 6.5 SEM with EDX analysis of spent CoMo/γ-Al_2O_3 catalyst after 19.1 h (IR).

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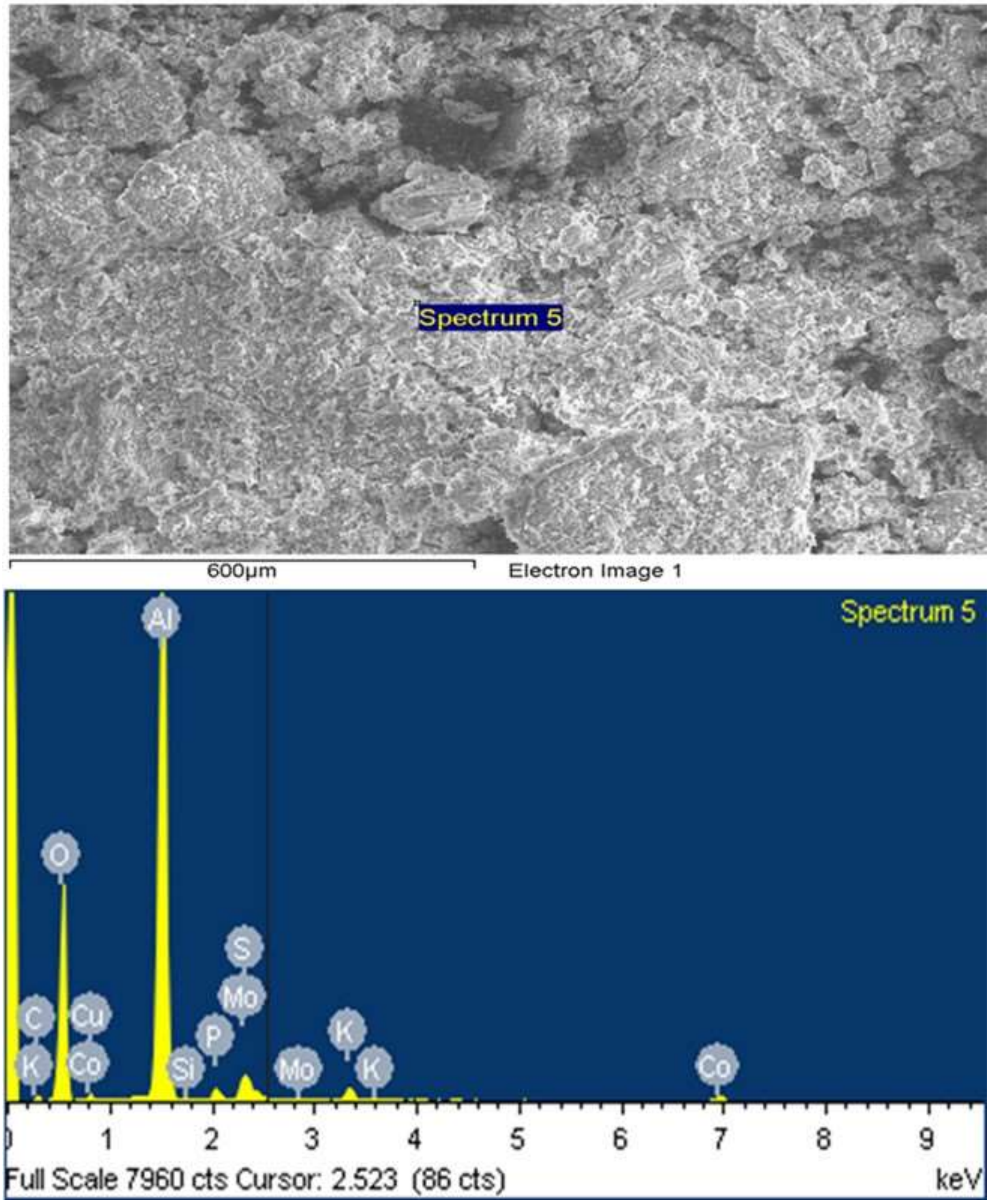

Figure 6.6 SEM with EDX analysis of spent CoMo/γ-Al_2O_3 catalyst after 12.2 h (R1).

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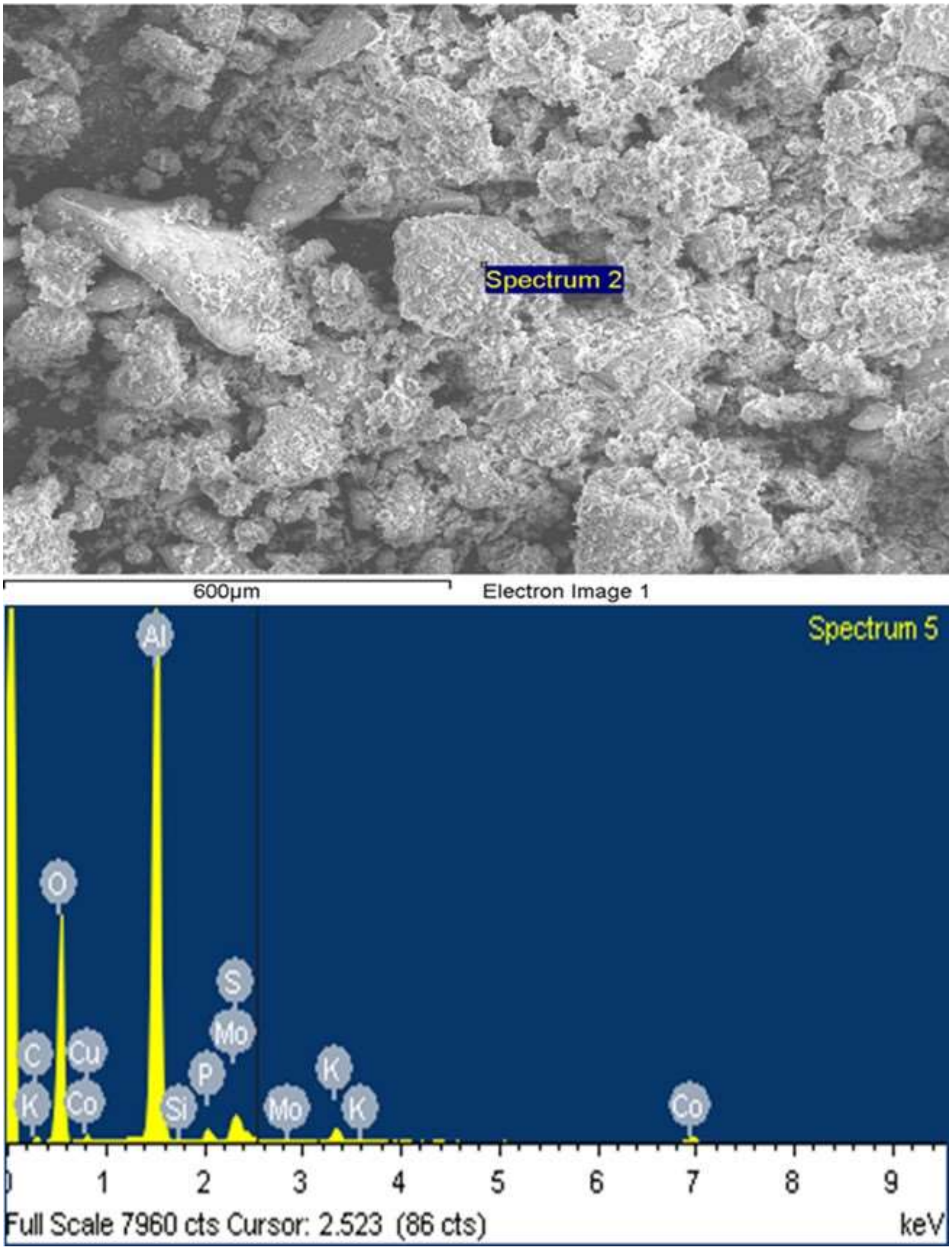

Figure 6.7 SEM with EDX analysis of spent CoMo/γ-Al_2O_3 catalyst after 16.5 h (R2).

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6.4.3.3 Thermogravimetric Analysis (TGA)

TGA was performed on the used catalysts to determine the amount of residual carbon deposited on the catalyst surface. A Shimadzu instrument TGA-50 was used to perform the TG analysis. A required amount of catalyst was placed in an alumina pan and a temperature program was ramped up at a rate of 5 °C/min starting at room temperature and terminating at 800 °C. The runs were performed under air flow of 50 mL/min. The percentage weight loss of the fresh CoMo/γ-Al_2O_3, fresh sulfided CoMo/γ-Al_2O_3 and those of spent CoMo/γ-Al_2O_3 catalyst from the PTBO 2 feedstock (showed better properties, yields and run time in comparison to RBO 0 and PTBO 1 feedstocks) are shown in Figures 6.8, 6.9, 6.10, 6.11 and 6.12.

Figures 6.8, 6.9, 6.10, 6.11 and 6.12 show significant loss during the intial heating period at the temperature range between 100 to 220 ºC. This weight loss was due to the removal of moisture from the catalyst surface and also moisture from the interior of the pores. Part of the weight loss could also be due to the removal of easily oxidizable carbonaceous species formed during initial decomposition of the aromatic compounds. Further the water which was bound with the catalyst material requires higher temperature for desorption. In the case of TGA analysis of fresh CoMo/γ-Al_2O_3 (Figure 6.8) and fresh sulfided CoMo/γ-Al_2O_3 (Figure 6.9) no weight loss was observed due to carbon deposition. However, in the case of spent CoMo/γ-Al_2O_3 (Figure 6.10) catalyst weight loss was expected but, in contrast, not much weight loss was observed only 1.8 mg of weight loss was observed at temperature between 418 to 563 °C. In the case of spent CoMo/γ-Al_2O_3 (Figures 6.11 and 6.12) catalyst weight loss was expected but, in contrast, not much weight loss was observed; only 0.15 and 0.1 mg of weight loss was observed at

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a temperature between 305 to 470 and 525 to 689 °C, which indicates that there was very little or negligible carbon deposition on the surface of the catalyst. More catalyst loss (1.8 mg) was observed in the case of IR (Figure 6.10), due to increased run time and more coke formation.

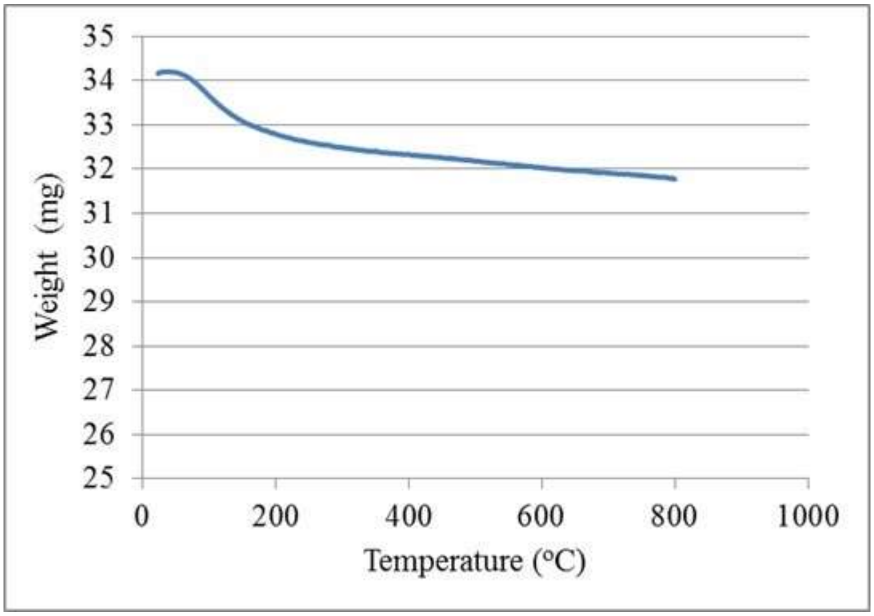

Figure 6.8 TGA of the fresh CoMo/γ-Al_2O_3 catalyst.

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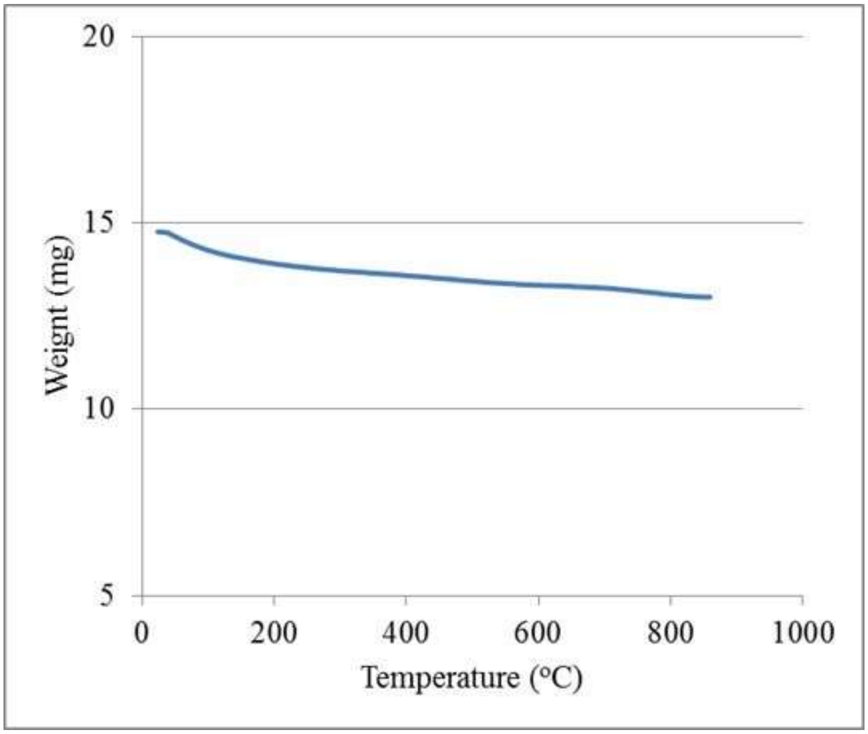

Figure 6.9 TGA of the sulfided CoMo/γ-Al_2O_3 catalyst.

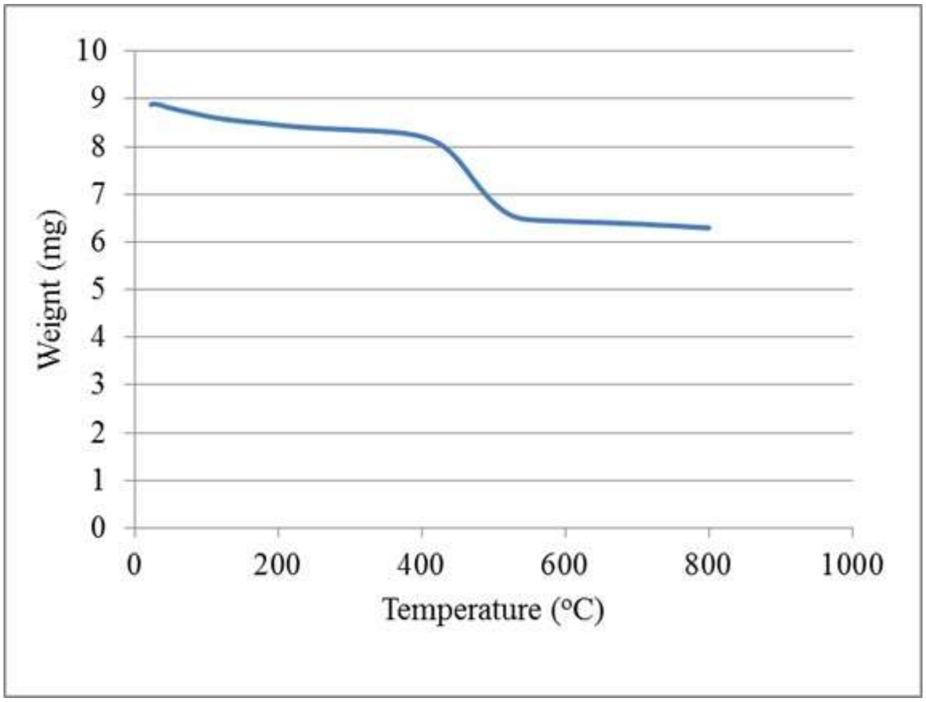

Figure 6.10 TGA of the CoMo/γ-Al_2O_3 catalyst after 19.2 h reaction time (IR).

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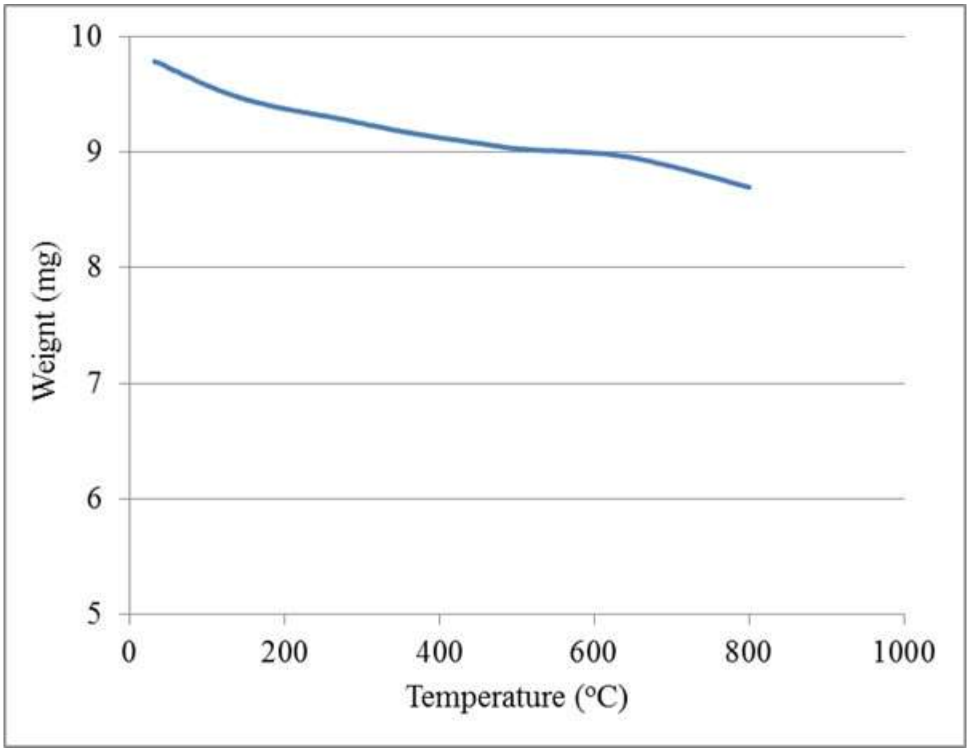

Figure 6.11 TGA of the CoMo/γ-Al_2O_3 catalyst after 12.2 h reaction time (R1).

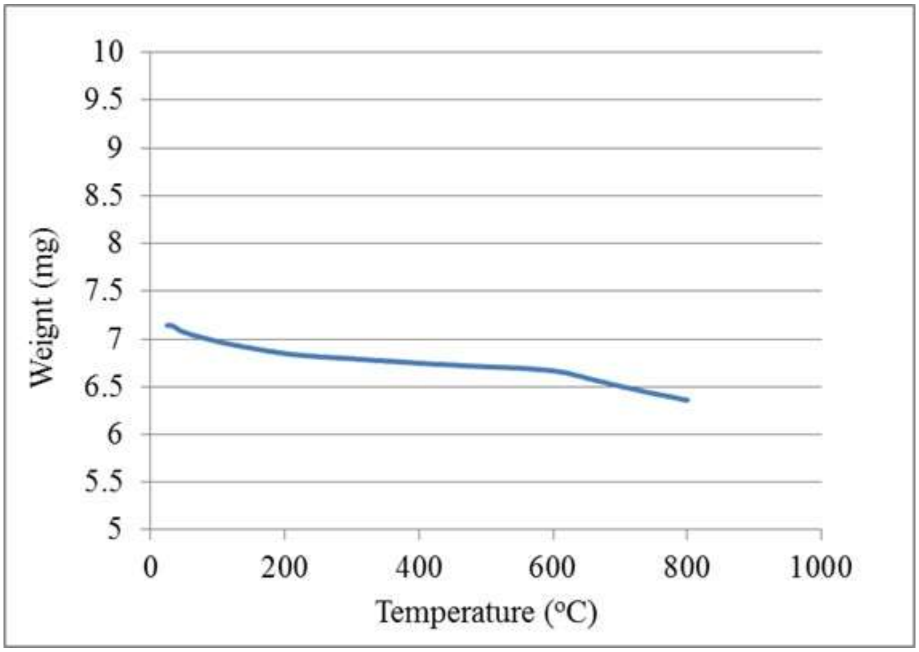

Figure 6.12 TGA of the CoMo/γ-Al_2O_3 catalyst after 16.5 h reaction time (R2).

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6.5 Conclusion

Table 6.22 provides a summary that includes OF property values for only total hydroprocessing run times for RBO 0, PTBO 1 and PTBO 2. Again, respective run times were 11.0, 12.1 and 19.2 h, respectively, for RBO 0, PTBO 1 and PTBO 2. It should be noted that the values in Table 6.20 are the total run time means comparison results previously produced in Table's 6.2, 6.3 and 6.4 for RBO 0, PTBO 1 and PTBO 2. The total run time properties in Table 6.20 were not compared among themselves. In addition to properties, run times and yields were also compared.

The AV's of treated RBO, PTBO 1 and PTBO 2 were 3.2, 3.1 and 3.0 mg KOH/g, respectively. Each of the feedstock AV's differed significantly among themselves. The significantly lowest AV of 3.0 mg KOH/g was obtained with PTBO 1 treatment for a run time of 12.1 h; the significantly next lowest AV of 3.1 mg KOH/g was obtained with PTBO 2 treatment for a run time of 19.2 h.

The HHV's of treated RBO, PTBO 1 and PTBO 2 were 40.8, 41.3 and 41.5 MJ/Kg, respectively. Each of the feedstock HHV's differed significantly among themselves. From the tested treatments the significantly highest HHV was obtained for PTBO 2 treatment followed by PTBO 1 treatment and then the RBO 0 treatment for respective run times of 12.1, 19.2 and 11.0 h.

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Table 6.22 Results (AV, HHV, oxygen content and WC % at 11.0, 12.1 and 19.2 h, TL, OF and AF) for feedstocks, RBO 0, PTBO 1 and PTBO 2 by hydroprocessing treatments.

Feedstock	RBO 0	PTBO 1	PTBO 2
Run time (h)	11.0 (C)	12.1 (B)	19.2 (A)
Property			
AV mg KOH/g	3.2 (A)	3.1 (C)	3.0 (B)
HHV MJ/Kg	40.8 (C)	41.3 (A)	41.5 (B)
Oxygen content (%)	7.7 (A)	3.4 (B)	2.3 (C)
WC (%)	2.6 (A)	0.9 (B)	0.3 (C)

The oxygen content of treated RBO, PTBO 1 and PTBO 2 were 7.7% for the11.0 h run time, 3.4% for 12.1 h and 2.3% for 19.2 h, respectively. Each of the feedstock oxygen content values differed significantly among themselves. The significantly lowest oxygen content of 2.3% was observed for the PTBO 2 treatment followed by PTBO 1 treatment with oxygen content of 2.8% and then by RBO 0 with an oxygen content value of 3.1%.

The WC percentage of treated RBO, PTBO 1 and PTBO 2 were 2.6% for the 11.0 h run time, 0.9 for 12.1 h and 0.3% for 19.2 h, respectively. Each of the feedstock WC percentages differed significantly among themselves. The OF from PTBO 2 treatment had the significantly lowest WC value of 0.3% among the tested treatments, which may be due to the presence of low water content in the untreated control PTBO 2. The next lowest WC value was 0.9% for PTBO 1 with the WC of RBO 0 being considerably higher at 2.6%.

Table 6.23 decribes the yields including TY, OF and AF for treated RBO 0, PTBO 1 and PTBO 2. The TY, OF and AF yields obtained with RBO 0 treatment were

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76.8, 16.4 and 60.4 wt% respectively. Each of the feedstock yield percentages differed significantly among themselves. For PTBO 1 treated TY yields were 86.1%, while the OF and AF yields were 18.7 and 67.4 wt% respectively. PTBO 2 treatment yielded a TY of 82.3, OF of 30.0 and AF of 52.3 wt% respectively. From the tested treatments PTBO 2 treatment yielded the significantly lowest AF yields of 52.3 wt% and significantly higher OF yields of 30.0 wt%.

Table 6.23 Yields (TL, OF and AF) for feedstocks, RBO 0, PTBO 1 and PTBO 2 by hydroprocessing treatments.

Yields (wt%)	RBO 0	PTBO 1	PTBO 2
TY	76.8 (C)	86.1 (A)	82.3 (B)
OF	16.4 (C)	18.7 (B)	30.0 (A)
AF	60.4 (B)	67.4 (A)	52.3 (C)

Among the tested treatments better properties were obtained with PTBO 1 and PTBO 2 in comparison to RBO 0. The longest run time of 19.2 h was observed for PTBO 2. For this longest run time for PTBO 2 the oxygen content and WC were the lowest as compared. However, in terms of AV and HHV, the values are slightly lower than the AV and HHV values of PTBO 1. But PTBO 2 was still considered as a better feedstock than PTBO 1 and RBO 0 with respect to run time and OF yields. The reason for better performance of PTBO 2 feedstock was due to the conversion of most of the oxygenated compounds into acids on pretreatment with oxone and hydrogen peroxide, followed by butyric anhydride addition. By this process of pretreatment water content and oxygen content reduction was more in comparison to PTBO 1 and RBO 0 feedstock.

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Table 6.24 provides a summary that includes OF property values for only total hydroprocessing run times for RBO 0, PTBO 1 and PTBO 2 for initial run and first and second regeneration. The values in Table 6.22 are the total run time means comparison results previously produced in Table's 6.2, 6.3, 6.4, 6.5, 6.6, 6.10, 6.11, 6.16 and 6.17's for RBO 0, PTBO 1 and PTBO 2 properties and yields (TY, OF and AF). The total run time properties in Table 6.22 were not previously compared between feedstock types.

The AV's of treated RBO 0, PTBO 1 and PTBO 2 following the initial fresh catalyst run were 3.2, 3.1 and 3.0 mg KOH/g, respectively. Each of these feedstock AV's differed significantly among themselves. The significantly lowest AV of 3.0 mg KOH/g was obtained for the PTBO 2 treatment at a run time of 12.1 h; the significantly next lowest AV of 3.1 mg KOH/g was obtained with PTBO 1 treatment for a run time of 19.2 h. The highest AV was for the RBO 0 treatment with an AV of 3.2 for a run time of 11.0 h.

The AV's of treated RBO 0, PTBO 1 and PTBO 2 following first catalyst regenration were 3.2, 3.1 and 1.3 mg KOH/g, respectively. Each of these feedstock AV's differed significantly among themselves. The significantly lowest AV of 1.3 mg KOH/g was obtained for the OF from the PTBO 2 treatment for a run time of 12.1 h; the significantly next lowest AV of 3.1 mg KOH/g was obtained with PTBO 1 treatment for a run time of 8.5 h; and the highest AV was for the RBO 0 treatment with an AV of 3.2 mg KOH/g for a run time of 7.1 h.

The AV's of treated RBO, PTBO 1 and PTBO 2 following second regeneration were 3.7, 3.2 and 1.4 mg KOH/g, respectively. Each of these feedstock AV's differed significantly among themselves. The significantly lowest AV of 1.4 mg KOH/g was

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obtained for the PTBO 2 treatment for a run time of 16.5 h; the significantly next lowest AV of 2.0 mg KOH/g was obtained with PTBO 1 treatment for a run time of 10.0 h; and the highest AV was for the RBO 0 treatment with an AV of 3.7 mg KOH/g for a run time of 10.0 h.

The HHV's of treated RBO, PTBO 1 and PTBO 2 following the initial run were 40.8 MJ/Kg 41.3 and 41.5 MJ/Kg, respectively. Each of these feedstock HHV's differed significantly among themselves. From the tested treatments the significantly highest HHV of 41.5 MJ/Kg was obtained for the PTBO 2 treatment for a run time of 19.2 h followed by the PTBO 1 treatment with a HHV of 41.3 MJ/Kg for a run time of 11.0 h and thenext lowest HHV was for the RBO 0 treatment with an HHV of 40.8 mg KOH/g for a run time of 11.0 h.

The HHV's of treated RBO, PTBO 1 and PTBO 2 following first regeneration were 40.1, 40.6 and 41.4 MJ/Kg respectively. Each of these feedstock HHV's differed significantly among themselves. From the tested treatments the significantly highest HHV of 41.4 MJ/Kg was obtained for the PTBO 2 treatment for a run time of 12.2 h followed by PTBO 1 treatment with a HHV of 40.6 MJ/Kg for a run time of 8.5 h and thenext lowest HHV was for the RBO 0 treatment with an HHV of 40.1 mg KOH/g for a run time of 7.1 h.

The HHV's of treated RBO, PTBO 1 and PTBO 2 following second regeneration were 40.0, 40.1 and 40.9 MJ/Kg respectively. Each of these feedstock HHV's differed significantly among themselves. From the tested treatments the significantly highest HHV of 40.9 MJ/Kg was obtained for the PTBO 2 treatment for a run time of 16.5 h followed by PTBO 1 treatment with a HHV of 40.1 MJ/Kg for a run time of 10.0 h; the

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next lowest HHV was for the RBO 0 treatment with an HHV of 40.0 mg KOH/g for a run time of 10.0 h.

Table 6.24 Mean values of the AV, HHV, oxygen content and WC percentage of the OF product from treated RBO 0, PTBO 1 and PTBO 2 by hydroprocessing for IR, R1 and R2 of the sulfided CoMo/γ-Al_2O_3 catalyst.

Properties	IR RBO 0	R1 RBO 0	R2 RBO 0	IR PTBO 1	R1 PTBO 1	R2 PTBO 1	IR PTBO 2	R1 PTBO 2	R2 PTBO 2
Run time (h)	11.0 (C)	7.1 (C)	10 (B)	12.1 (B)	8.5 (B)	10.0 (B)	19.2 (A)	12.2 (A)	16.5 (A)
AV mg KOH/g	3.2 (A)	3.2 (A)	3.7 (A)	3.1 (B)	3.1 (B)	3.2 (B)	3.0 (C)	1.3 (C)	1.4 (C)
HHV MJ/Kg	40.8 (C)	40.1 (C)	40.0 (C)	41.3 (B)	40.6 (B)	40.1 (B)	41.5 (A)	41.4 (A)	40.9 (A)
Oxygen content (%)	3.9 (A)	4.1 (A)	5.3 (A)	3.4 (B)	3.5 (B)	5.2 (B)	2.3 (C)	2.5 (C)	4.6 (C)
WC (%)	2.6 (A)	2.7 (A)	4.4 (A)	0.9 (B)	1.1 (B)	4.1 (B)	0.3 (C)	0.8 (C)	2.9 (C)

Letters in parentheses indicate significant differences between property means as influenced by time interval.

The oxygen content of treated RBO 0, PTBO 1 and PTBO 2 following the initial catalyst run were 3.9% for the11.0 h run time, 3.4% for 12.1 h and 2.3% for 19.2 h, respectively. Each of these feedstock oxygen content values differed significantly among themselves. The significantly lowest oxygen content of 2.3% was observed for the PTBO 2 treatment followed by the PTBO 1 treatment with oxygen content of 2.8%; the highest oxygen content value was 3.1% for the RBO 0 treatment.

The oxygen content of treated RBO 0, PTBO 1 and PTBO 2 following first regeneration was 4.1% for the 7.1 h run time, 3.5% for 8.5 h and 2.5% for 12.2 h respectively. Each of these feedstock oxygen content values differed significantly among

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themselves. The significantly lowest oxygen content of 2.3% was observed for the PTBO 2 treatment followed by the PTBO 1 treatment with an oxygen content of 3.5% and then by RBO 0 with an oxygen content value of 4.1%.

The oxygen content of treated RBO 0, PTBO 1 and PTBO 2 following the second catalyst regeneration was 5.3% for the10.0 h run time, 5.2% for 10.0 h and 4.6% for 16.5 h respectively. Each of these feedstock oxygen content values differed significantly among themselves. The significantly lowest oxygen content of 4.6% was observed for the PTBO 2 treatment followed by PTBO 1 treatment with an oxygen content of 4.1% and then by RBO 0 with an oxygen content value of 4.4%.

The WC percentage of treated RBO 0, PTBO 1 and PTBO 2 following initial run was 2.6% for the 11.0 h run time, 0.9 for 12.1 h and 0.3% for 19.2 h, respectively. Each of these feedstock WC percentages differed significantly among themselves. The OF from PTBO 2 treatment had the significantly lowest WC value of 0.3% among the tested treatments. The next lower WC value was 0.9% for PTBO 1 with the WC for the RBO 0 treatment considerably higher at 2.6%.

The WC percentage of treated RBO 0, PTBO 1 and PTBO 2 following first regeneration was 2.7% for the 7.1 h run time, 1.1 for 8.5 h and 0.8% for 12.2 h, respectively. Each of these feedstock WC percentages differed significantly among themselves. The OF from PTBO 2 treatment had the significantly lowest WC value of 0.8% among the tested treatments. The next lowest WC value was 1.1% for PTBO 1, with the highest WC value of 2.7% for the RBO 0 treatment.

The WC percentage of treated RBO 0, PTBO 1 and PTBO 2 following second generation was 4.4% for the 10.0 h run time, 4.1 for 10.0 h run time and 2.9% for 16.5 h

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run time, respectively. Each of these feedstock WC percentages differed significantly among themselves. The OF from the PTBO 2 treatment had the significantly lowest WC value of 2.9% among the tested treatments. The next lowest WC value was 4.1% for PTBO 2 and the highest WC value was 4.4% for the RBO 0 treatment.

Table 6.25 decribes the yields summary including TY, OF and AF for treated RBO 0 PTBO 1 and PTBO 2 following initial run, first and second regeneration. For the initial run the TY, OF and AF yields obtained with RBO 0 treatment were 76.8, 16.4 and 60.4 wt% respectively. Each of these feedstock OF yield percentages differed significantly among themselves. For PTBO 1 treated TY yields were 86.1%, while the OF and AF yields were 18.7 and 67.4 wt% respectively. PTBO 2 treatment yielded a TY of 82.3, OF of 30.0 and AF of 52.3 wt% respectively. From the tested treatments PTBO 2 treatment yielded the significantly lowest AF yields of 52.3 wt% and significantly higher OF yields of 30.0 wt%.

For first regeneration the TY, OF and AF yields obtained with RBO 0 treatment were 78.2, 14.1 and 64.1 wt%, respectively. Each of these feedstock yield percentages differed significantly among themselves. For PTBO 1 treated TY yields were 73.7%, while the OF and AF yields were 10.4 and 63.3 wt%, respectively. PTBO 2 treatment yielded a TY of 65.0, OF of 16.2 and AF of 48.8 wt%, respectively. From the tested treatments PTBO 2 treatment yielded the significantly lowest AF yields of 48.8 wt% and significantly higher OF yields of 16.2 wt%.

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Table 6.25 Mean yields (TY, OF and AF) summary from treated RBO 0, PTBO 1 and PTBO 2 by hydroprocessing for IR, R1 and R2 of the sulfided CoMo/γ-Al_2O_3 catalyst.

Feedstock	IR RBO 0	R1 RBO 0	R2 RBO 0	IR PTBO 1	R1 PTBO 1	R2 PTBO 1	IR PTBO 2	R1 PTBO 2	R2 PTBO 2
Runtime	11.0	7.1	10.0	12.2	8.5	10.0	19.2	12.2	16.5
	Yields (Wt%)			Yields (Wt%)			Yields (Wt%)		
TY	76.8 (C)	78.2 (A)	80.1 (A)	86.1 (A)	73.7 (B)	71.0 (C)	82.3 (B)	65.0 (C)	71.5 (B)
OF	16.4 (C)	14.1 (B)	24.8 (B)	18.7 (B)	10.4 (C)	21.5 (C)	30.0 (A)	16.2 (A)	30.5 (A)
AF	60.4 (B)	64.1 (A)	55.3 (A)	67.4 (A)	63.3 (B)	50.5 (B)	52.3 (C)	48.8 (C)	41.0 (C)

Letters in parentheses indicate significant differences between property means as influenced by time interval.

For second regeneration the TY, OF and AF yields obtained with RBO 0 treatment were 80.1, 24.8 and 55.3 wt%, respectively. Each of these feedstock yield percentages differed significantly among themselves. For PTBO 1 treated TY yields were 71.0%, while the OF and AF yields were 21.5 and 50.5 wt%, respectively. PTBO 2 treatment yielded a TY of 71.5, OF of 30.5 and AF of 41.0 wt%, respectively. From the tested treatments PTBO 2 treatment yielded the significantly lowest AF yields of 41.0 wt% and significantly higher OF yields of 30.5 wt%.

Among the tested treatments better properties were obtained with PTBO 1 and PTBO 2 in comparison to RBO 0 after second regeneration. The longest run time of 16.5 h was observed for PTBO 2. For this longest run time for PTBO 2 the properties AV, oxygen content and WC were the lowest. The HHV values were higher than the HHV values of PTBO 1 and RBO 0. PTBO 2 was considered be a better feedstock than PTBO

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1 and RBO 0 with respect to properties, run time and OF yields even after second regeneration of the catalyst. From the above results, it was concluded that the sulfided CoMo/γ-Al_2O_3 catalyst performance was superior even after two regenerations with PTBO 2, than PTBO 1 and RBO 0. The reason for better performance of PTBO 2 feedstock was due to the conversion of most of the oxygenated compounds into acids and lower water content of the PTBO 2 on pretreatment with oxone and hydrogen peroxide, followed by butyric anhydride addition. By this process of pretreatment water content and oxygen content reduction was higher in comparison to PTBO 1 and RBO 0 feedstock.

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